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# SOIL SCIENCE

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## MAGNESIUM SYMPOSIUM

This issue of SOIL SCIENCE is devoted to a series of papers on magnesium, most of which were presented before the Division of Fertilizer Chemistry of the American Chemical Society at its annual fall meeting held at the Stevens Hotel in Chicago, Illinois, on Tuesday, September 10, 1946. The meeting was attended by some 150 chemists who were interested in knowing more about the magnesium needs of plants and the means by which an adequate supply of the element can be maintained in the soil. These papers give a fairly complete picture of the current status of our knowledge about the soil-plant interrelationships of magnesium. We are pleased to be able to present them for the benefit of the readers of this Journal.

FIRMAN E. BEAR.

### MAGNESIUM IN PLANTS<sup>1</sup>

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Magnesium is one of the elements essential to plant growth. Its specific functions within the plant and the mechanisms operating to fulfill these functions are not as yet fully established. This paper includes observations that have been recorded on this aspect of the problem as well as those bearing on the quantity of and need for Mg in plants and on Mg absorption by plants as affected by other ions.

#### ROLE IN PLANT CONSTITUENTS AND PROCESSES

##### *Chlorophyll*

✓ Mg comprises 2.7 per cent of the chlorophyll molecule, of which it is an essential constituent (68). The characteristic Mg-deficiency symptom is an interveinal chlorosis of the leaves of the plant that starts at their edges and gradually spreads in toward the center with increasing intensity of the deficiency. Rabinowitch (56) observed that Mg deficiency adversely affected the formation of chlorophyll and, indirectly, photosynthesis. Much more Mg was required to bring about a full rate of photosynthesis than was necessary to prevent chlorosis. Marneli (41) found that the ash of green leaves contained a higher percentage of Mg than did the ash of chlorotic leaves of the same plant. In studying the effect of Mg on the development of chlorophyll in algae, corn, sunflower, and buckwheat, this author found that the amount of coloring matter extracted was in direct proportion to the Mg content of the culture solution. Javillier and associates (35) found that chlorophyll Mg represented only about 10 to 30 mgm. per 100 gm. dry weight of leaves of 22 plants. The ratio of chlorophyll

<sup>1</sup> Journal Series paper of the New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

Mg to that of total leaf Mg ranged from 0.8 to 26 in the leaves of nine of these plants. They concluded that chlorophyll Mg represented only a very small fraction of total leaf Mg.

Longnecker<sup>2</sup> found a significant correlation between chlorophyll and Mg concentrations in the leaves of five strains of corn. Aside from the Mg contained in the chlorophyll, however, there was no close relationship between chlorophyll concentration and total Mg content of the leaves. With short-lived radioactive Mg as a tracer, Ruben and associates (54) made an unsuccessful attempt to detect the interconversions of chlorophylls "a" and "b" during photosynthesis. Purified crude mixtures of the two chlorophylls took up radioactive Mg, but the separated components did not effect an exchange of their Mg with the radioactive Mg ion in an 80 per cent acetone solution. Using the figure of Willstatter and Stoll that the average content of chlorophyll in green leaves was about 0.8 per cent of the total dry weight, Garner and associates (9) concluded:

It is evident that in order to prevent breaking down of chlorophyll the total Mg content of the leaf must be several times the quantity present in the chlorophyll.

#### *Phosphate carrier*

By acting as a carrier of phosphates, Mg is believed to be closely related to phospholipid formation and to the synthesis of nucleoproteins in plant cells (36). In support of this theory is the evidence that Mg is abundant in young meristematic plant tissue, in the seed, and in the fruit. Truog and associates (60) investigated the relationship of the supply of available Mg to the P content of pea seed by means of field and nutrient culture tests in which the supplies of available Mg and P were varied. Consistent increases in P content occurred with increasing supplies of available Mg, the P content of the seeds being increased much more by the use of extra Mg than of extra P. They concluded that greater attention should be given to supplies of available Mg in soils in order that the P present in the soil might be used more effectively. These authors suggested that failures to obtain crops of higher P content through the addition of phosphate fertilizers may have been due to a lack of available Mg.

Bartholomew (3) also noted that plants took up increased amounts of P when additional Mg was supplied. Bernadini and associates (6) and MacGillivray (39) discussed the redistribution of Mg within the plant structure in relation to the migration of P from one organ to another, particularly from the seed piece to that portion of the growing plant in which it was to be used. Eckerson (22) found that as the inorganic P in tomato plants was used up the chloroplasts in the stem and lower leaves disintegrated. As the plant phosphatids were partially freed and broken down, the chloroplasts in the upper leaves began to be affected. Only if additional P was added during the first stage of the process was recovery of the plant possible. Carolus (14) pointed out that only 10 per

<sup>2</sup> Longnecker, T. C. A study of the relation between chlorophyll and mineral contents of corn leaves and plant yields. 1941. [Unpublished doctor's thesis. Copy on file Rutgers Univ. Library, New Brunswick, N. J.]

out of the Mg in the green part of the plant was found in the chlorophyll. The remainder assisted in initiating new growth. Scharrer and Schreiber (55) reported that although a mixture of  $K_2SO_4$  and  $MgSO_4$  did not increase the protein content of seed of summer rape over that of  $K_2SO_4$  alone, the fat content of seed increased as increasing amounts of Mg were supplied. With dodder seed, however, increasing amounts of K alone caused a greater decrease in percentage fat content than that produced by the addition of K and Mg.

### *Seed*

The fact that Mg is concentrated in the seed and fruit of plants follows as a corollary to its phosphate-carrying role, and the relation of the phosphates to oil and protein formation. Loew (36) found an unusually high percentage of Mg in oily as compared to starchy seeds, the ratio being about 5:2. Willstätter (67) noted that the Mg content of cereal seeds always exceeded the content of Ca and that the Mg content of the seed commonly exceeded that of its cover. The nutritive tissues of the seed frequently contained more Mg than did the green assimilating parts of the plant. During ripening of the seed, a progressive increase in Mg and P content occurred with a simultaneous decrease in total ash.

Reed and Haas (52) found that the translocation of Mg from old leaves to those newly developing was not so pronounced as that to the fruit. Fudgo (26, 27, 28) demonstrated the effect of fruit production in developing Mg-deficiency symptoms on citrus leaves. He established that Mg deficiency was associated with seediness (25). In the summer Mg was translocated from the leaves to nearby fruit until by fall it was so low that chlorosis developed and the leaves finally dropped from the trees.

### *Carbohydrate production and transport*

Raumer (61) was the first to suggest that Mg was involved in the transfer of the starch from leaves to stems. Subsequently a number of investigators concluded that a relation existed between Mg and the transfer of carbohydrates in plants. It is known that phosphates act as the coenzyme of zymase, and there is also some evidence that P is necessary for the transformation of starch to sugar. Whether Mg is related to carbohydrate production and transport by virtue of the phosphate-carrying role or through another mechanism is not clear.

John and Bougy (17) found that sugar beets contained a much larger proportion of Mg than the food varieties. In the early stages of development the chemical composition was the same with both types, the differences being manifested as the sugar reserves accumulated. Vladimirov and associates (62) suggested that Mg increased the sugar content of beets but that the element played no part in the transfer of monosugars from the leaves to the roots.

Garner and associates (29) analyzed Mg-deficient tobacco leaves and found that they contained less carbohydrates than normal leaves. Shvyndenkov (57) noted that the yield and sugar content of sugar beet roots in sand cultures were higher following the addition of the chlorides of Na and Mg than of their sulfates. The contents of Ca, Mg, and K were also higher following the addition



of chlorides than sulfates. Similarly the addition of  $MgCl_2$  increased the content of maltose-like carbohydrates. Van Koot and Pattje (61), working with Mg-deficient tomatoes, found that low carbohydrate content was associated with low Mg.

### *Aging of plants*

Egorov (23) noted that the theory of aging of plants rested on the assumption that certain organs, probably the leaves, became depleted of one or more of their essential constituents, especially Mg, as a result of their being stored in other organs, the seed in particular. Lutman and Walbridge (37) elaborated on this theory of "exhaustion of organs," maintaining that the withdrawal of Mg from the older leaves resulted in the destruction of their chlorophyll and led to yellowing, premature aging, and eventual death of the plant. The authors concluded, however, that

Mg probably plays a secondary part in the senescence of plants. Its lack may be one of the factors concerned therein, but probably many other complicated internal disturbances and rearrangements are responsible for all the phenomena associated with normal ageing in plants.



### *Accumulation of nitrogen in legumes*

Albrecht (1) showed that when no Mg was added to the nutrient medium, fixation was insignificant unless extra Ca was available. As more Mg was added, fixation increased. He suggested that nodule bacteria were acclimated to plants that were accustomed to a high level of soil fertility in the form of Ca, Mg, and other mineral nutrients. Mg also had an indirect effect in that it appeared to function in the release of Ca, which was absorbed by the plant with resulting increase in nitrogen fixation. Graham (31) showed, in addition, that Mg increased the fixation of nitrogen by soybean plants by stimulating bacterial activity to a much greater degree than did equal quantities of Ca compounds.

### *Miscellaneous*

A number of additional roles have been ascribed in whole or in part to Mg. Lutman (38) observed that a lack of balance of Mg, as well as of N, P, K, and Ca, would be noted in the general habit of growth of a plant and in the structure of the cells themselves. Any abnormality in the supplies of these elements influenced the susceptibility of cellular tissues to infection by disease organisms. Bledsoe and associates (7) found leafspot of peanut to be associated with Mg deficiency. In growing peanut plant roots in solutions from which P, K, Ca, S, and Mg were withdrawn singly, the Mg-deficient cultures were the only ones that developed the disease to any appreciable extent. Whether or not the severity of the leafspot disease could be reduced by higher levels of Mg still is to be determined.

Vladimirov (63) made a comparison of the effects of K, Na, and Mg upon the storage of caoutchouc, the economically valuable reduction product in kok-saghyz roots. He found that Mg brought about a pronounced stimulation of

the reduction processes in the plant and markedly increased the accumulation of this constituent. It was suggested that the use of ammonium salts with K and Mg sulfates might increase the content of other reduced products, such as the volatile oils in essential-oil plants and pyrethrin in the Dalmatian daisy. The greatly increased fat content of sunflower seeds with Mg additions was likewise connected with the stimulation of the reduction processes in the plant (42).

#### QUANTITY OF AND NEED FOR MAGNESIUM IN PLANTS

Mg is present in plants in at least three states: in combined form in the protoplasm, in a specific linkage in the chlorophyll molecule, and in a free or inorganic salt form in the cell sap. The quantity of Mg needed differs for the various plant species. Beeson (4) and Orr (47) included Mg in their excellent general compendia on the mineral composition of crops. Beeson made special reference to the relation between the composition of soils and that of the crops growing on them. He recorded the percentage content of Mg in the various organs of some 60 plant species, each grown on several soil types and harvested at various stages of maturity. Orr dealt mainly with pasture plants in relation to animal nutrition. He concluded that the amount of Mg present in pasture herbage was probably always more than sufficient to meet the requirements of the animals grazing upon them.

Bender and Eisenmenger (5) classified certain plants on the basis of their sensitivity to soil acidity and showed that they generally contained higher percentages of Mg when grown on basic than on acid soils. Legumes were found to contain the highest percentages of Mg, and small grains, the lowest. Colander (18), in a study of the selective absorption of cations by plants, found that the several species varied in their capacity for selective accumulation of Li, Mg, Ca, and Sr, the maximum absorption being three to five times greater than the minimum. He demonstrated that the Chenopodiaceae and the members of the Fagopyrum family were always rich in Mg, whereas Pisum, Vicia, and Avena were relatively poor in this element.

After experimental work involving a large variety of plant species, Eisenmenger (24) found that families of seed plants in the lower stages of evolutionary development always had high Mg requirements. Among the highly developed plants, however, none showed Mg-deficiency symptoms except corn, potatoes, and some of the cucurbits. Brown and Hollowell (12), in their review of the literature on the chemical composition of some pasture and hay plants as affected by soils and fertilizers, found few reported instances of Mg deficiency. Daniel (20) analyzed composite samples of 162 mature grasses and legumes from typical areas of native pastureland and of hay from virgin soils in 35 counties of Oklahoma. The average Mg content of 19 different species of grasses was 0.156 per cent, sorghum containing the highest percentage of Mg, and love grass (*Eragrostis curtipedicellata*), the lowest. Six different species of mature legumes averaged 0.379 per cent Mg, peanut vines having the highest and velvet beans the lowest percentages. The legumes contained 2.43 times as much Mg as the grasses. In both the grasses and legumes, Mg was present in greater abundance

than P but in smaller quantities than Ca and N. In attempting to explain why legumes contained higher percentages of Mg than nonlegumes, Newton (44) observed that the roots of pea plants gave off more CO<sub>2</sub> than did those of barley plants. Because of the effect of this extra CO<sub>2</sub> on the solubility of soil Ca and Mg compounds, pea plants absorbed more of the alkaline earths than did barley plants.

Several experiments have been carried out to determine how and to what degree the nutrient needs of plants change during their life cycle. Gericke (30) found that when wheat seedlings, after 4 weeks' exposure to complete nutrient solutions, were transferred to media devoid of Mg they produced markedly more straw and grain than plants that grew to maturity in complete nutrient solutions thrice renewed. Exposure of cultures to complete solutions for more than 4 weeks before transfer to media devoid of Mg was inhibitory to the maximum development of the plants. Thus in evaluating the nutrient requirements of a plant both the rate of supply of salt elements and the plant's physiological needs should be considered.

Daniel (20) determined the Mg content of legumes at weekly intervals for 7 weeks and concluded that the percentage in both roots and tops decreased as the plant matured. Borst and Thatcher (8) found that as soybean plants matured the Ca, Mg, K, and P contents of the stems decreased. In the leaves, however, Mg remained fairly constant. Nelson and associates (43) demonstrated that the maturity of soybeans was retarded by additions of K or Mg. Hawkins (32) found that the Green Mountain potato plant absorbed approximately 7 per cent of its total Mg during the first 50 days of growth, an additional 60 per cent during the next 30 days, and the remaining 33 per cent during the last 30 days. These percentages were somewhat lower than those of the major nutrients during the first and second time intervals. During the last period, however, the rate of absorption of Mg was greater than that of the major nutrients. In terms of proportion of the season's growth completed, these time intervals corresponded to 3, 48, and 49 per cent, respectively. In another experiment (33) the tomato plant was found to absorb 3 per cent of its total Mg during the first month of growth, 20 per cent during the second month, and 77 per cent during the last month. Somewhat greater percentages of Ca and K than of Mg were absorbed during the second month. Carolus (15) concluded that rapidly growing crops, such as potatoes, cabbage, spinach, cucumbers, and corn, had definite periods in their growth during which their Mg requirement was very high. If an abundance of the element was not available at that time, chlorosis occurred in the lower foliage. The potato plant, for example (16), had its maximum nutrient requirement during the period between the fiftieth and the eightieth day after planting.

Olson and Bledsoe (46) showed that the proportion of Mg absorbed by the cotton plant in relation to that of P was greater at the start of the growing period than at its conclusion. Stubblefield and DeTurk (59) demonstrated that the Mg in the corn plant is concentrated mainly in the stalks, the Mg percentage in the stover being about three times that of the grain. In wheat and oats, the

allocation of Mg between grain and straw was approximately equal. The percentages of Mg in the grain of the three species were about equal, variations in Mg absorbed as a result of differences in the soil's supply of the element being more evident in the vegetative organs. Fudge (27) reported that citrus tree foliage contained  $1\frac{1}{2}$  times as much Mg as P, whereas the fruit contained only about three-fourths as much. Mg was thus required in quantities at least as great as those of P. Rigg and associates (53) reported that in apple trees suffering from Mg deficiency the young leaves at the tip of the current season's leader growth contained about twice as much Mg as the oldest leaves at the base of the leader. In Mg-sufficient trees the Mg content of the leaves was approximately the same in all parts of the leader. In Mg-deficient trees the Mg content of the wood from leader growth was slightly lower than that of the leaves. In healthy trees the Mg content of leader wood was about half that of the leaves.

TABLE 1  
*Critical percentages Mg below which Mg deficiencies were manifested*

PLANT	ORGAN ANALYZED	PERCENTAGE Mg	AUTHORITY
Potato	Foliage	0.15	Brown <i>et al.</i> (13)
Potato*	Lower leaves	0.24	Carolus (14)
Apple	Mature leaves	0.15	Boynton (11)
Citrus	Leaves	0.30	Fudge (28)
	Whole fruit	0.12	Fudge (28)
	Seed	0.19	Fudge (28)
Tomato	Leaves	0.20-0.31	Walsh <i>et al.</i> (65)
Tung	Leaves	0.20-0.35	Drosdoff (21)
Potato	Leaves	0.17-0.38	Walsh <i>et al.</i> (66)
Tobacco	Leaves	0.06	Walsh <i>et al.</i>
Sugar beets	Leaves	0.05 (0.20 in field)	Walsh <i>et al.</i>
Barley	Straw-grain	0.05	Walsh <i>et al.</i>
Mangold	Leaves	0.22-0.43	Walsh <i>et al.</i>

\* Irish cobbler.

Table 1 presents some accumulated data on critical percentages of Mg in plants. In tissues containing less than these defined limits, Mg-deficiency symptoms developed either in the guise of a chlorosis or of decreased growth.

#### MG ABSORPTION BY PLANTS AS AFFECTED BY OTHER IONS

Soil-plant literature contains many examples of the depressing effect of high concentrations of Ca and K, particularly the latter, on plant absorption of Mg. Thus Walsh and Clarke (65) noted that the K:Mg ratio in the soil determined the degree of Mg uptake in tomatoes. If the ratio was sufficiently high, chlorosis developed even when the culture medium had a relatively large content of available Mg. MacGregor and Rost (40) found that although naturally high Ca- and Mg-carbonate concentrations in the soil had little effect on K concentrations in the tissue of potato plants, the amounts of Ca and Mg absorbed were greater than in plants growing on low-carbonate soils.

Hunter<sup>3</sup> found that alfalfa plants grown on soils with a constant level of Mg showed increased percentages of Mg with increasing Mg:K ratios. Further study of his data revealed that Mg uptake by the plant increased with increasing Ca:K ratios in the exchange complex. The data also showed that with successive alfalfa harvests, plant absorption of Mg increased from 0.28 per cent in crop 1 to 0.42 per cent in crop 7. This increase coincided with decreased supplies of available K in the soil. In working with potatoes, tobacco, sugar beets, barley, and mangold plant tissue, Walsh and O'Donohoe (66) noted that where Mg deficiency was apparent in plants an extremely high quantity of exchangeable K was present in the soil. According to Barnes (2), potatoes growing on an acid soil derived little benefit from a K application unless the supply of soil Mg was adequate.

Wallace and associates (64) grew potatoes on plots on which a fertilizer experiment on black currants had been in progress from 1927 to 1941 and found that K-deficiency symptoms were prevalent on the leaves where K had not been applied, and Mg-deficiency symptoms, where it had. Mg-deficiency symptoms were less evident where farmyard manure had been used. Southwick (58) presented evidence that K fertilization so raised the level of available K in some apple-orchard soils as to bring about an actual shortage of Mg, the deficiency manifesting itself in the form of leaf-scorch. He questioned the advisability of using K for apple orchards until the Mg supply was built up. Boynton and Compton (10) pointed out that in orchards showing Mg-deficiency symptoms leaf K tended to be abnormally high even though the amount of replaceable K in the soil was low and no K supplements were used. They suggested that since high leaf K was often a sign of Mg deficiency, analyses for both K and Mg were helpful in the diagnosis of Mg deficiency.

Pierre and Bower (48) found that Ca had less effect than Mg in depressing K absorption. Shive (56) studied the growth of wheat plants at 36 Ca:Mg:K ratios each at osmotic concentrations of 0.1, 1.75, and 4.0 atmospheres. He concluded:

For any given set of salt proportions, the total concentration of the medium determines the growth of plants. . . . The values of the cation ratios Mg:Ca, Mg:K, and Ca:K appear to determine the growth of plants in many cases, but this relation is not always clear for any single ratio; it generally requires two of these ratio values to determine the physiological properties of the nutrient solutions with any given total concentration.

In a study of the Mg status of 20 New Jersey soils, Prince, Zimmerman, and Bear (49) concluded:

The most significant single factor influencing the Mg uptake of alfalfa plants is the quantity of K that is available for their use . . . . As the K supply decreases with repeated harvests of a crop like alfalfa the Mg content of the plant increases, even when it is growing on a soil that is very deficient in Mg . . . . Lack of correlation between critical Ca:K

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<sup>3</sup>Hunter, A. S. Calcium-potassium interrelationships between the soil and the alfalfa plant. 1942. [Unpublished doctor's thesis. Copy on file Rutgers Univ. Library, New Brunswick, N. J.]

ratios in the plant and plant yields may occur when sufficient Mg is available in the soil to serve as a partial substitute for K if the latter element is present in very low amounts . . . . If Mg constitutes less than 6 per cent of the exchange cations in a soil, crops growing on that soil are likely to respond markedly to applications of the element in soluble form . . . . It is doubtful whether 80 pounds available MgO per ton of fertilizer is adequate to meet the needs of crops where high-K fertilizers are applied to soils that are low in exchange Mg.

Zimmerman<sup>4</sup> studied the effect of variations in absolute and relative concentrations of exchangeable Ca, Mg, and K in a soil on plant growth, and concluded:

At higher levels of fertility, Ca can be harmful unless accompanied by adequate Mg. The Mg is needed not only for Ca balance but, more especially, to overcome high K concentrations . . . . Increasing concentrations of soil Mg do not result in an increased Mg uptake by the plant if the absolute quantities of K present are sufficiently high . . . . Although uptake of Ca and K is closely related to their total concentrations, plant absorption of Mg usually bears a straight line relationship to exchange Mg:K ratios in the soil . . . . At low fertility levels plant uptake of Mg is closely related to the available supplies of the element. At higher fertility levels the cation ratios play a more dominant role. It is at these higher levels that adequate supplies of Mg are especially important.

Wilson (69) reported that the relative intensity of removal of cations from soil by electrodialysis correlated with the strength of the ions, namely:  $K > Na > Ca > Mg$ . Cooper (19) showed that many plants selectively absorbed the relatively strong ions, the quantities of Mg in most plants being significantly lower than those of K or Ca. He found that the standard electrode potentials, ionization potentials, and the solubility of Mg compounds were useful in interpreting Mg uptake by plants.

Relatively few reports have appeared on the influence of elements other than Ca and K on Mg absorption. Walsh and Clarke (65) recorded that a low level of S nutrition retarded development of Mg-deficiency chlorosis by enhancing Mg uptake. Obenshain (45) reported that as the supplies of N were increased for corn, the tissues contained more Mg. Hoblyn (34) demonstrated that Mg-deficient trees under high-N fertilization showed less leaf-scorch than trees receiving less N or none at all. Boynton and Compton (9) found a positive correlation between leaf N and leaf Mg in trees differentially fertilized with N. Olson and Bledsoe (46) noted a nearly constant relationship of twice as much N as MgO throughout the vegetative and reproductive organs of cotton.

From the foregoing review of literature on Mg relationships in plants, it is apparent that a great deal of fundamental work is yet to be done on this highly important topic. It is hoped that in pointing out the need, this review may be of value to future investigators in this field of research.

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# RELATIONSHIP OF SEED PLANT DEVELOPMENT TO THE NEED OF MAGNESIUM<sup>1</sup>

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The relationship of seed plant development to magnesium needs can be well understood only if trials are made of individual species, for not all species of a family behave alike.

To study the behavior of plants to deficiencies of magnesium, a 1-acre plot at the Massachusetts Station, known to be deficient in magnesium, was divided into four equal areas. To these, additions were made as follows: first area, neither calcium nor magnesium; second area, magnesium; third, magnesium and calcium; and fourth, calcium alone. The calcium was added in the form of ground nondolomitic limestone at the rate of 1000 pounds per acre. The magnesium was added as the sulfate at the rate of 150 pounds per acre. This treatment gave one area with a low pH and one with a high pH, each deficient in magnesium. Potassium was added in the form of the chloride, and phosphorus as ammophos. Additional nitrogen was supplied from sodium nitrate.

It was found from many studies that the families of seed plants in the lower stages of evolutionary development always show magnesium needs. Some of the intermediate families also show symptoms of magnesium deficiency. Among the extremely highly developed plants, none show the deficiency except a few isolated members that may have been greatly changed by man through domestication and hybridization. Among these is corn. Potatoes and one or more species of cucurbita, which do not belong to the most highly developed group but which are, nevertheless, fairly well developed plants, may also be included.

The concept of plant evolution has been received with universal scientific accord, but the details regarding the place of seed plants in the scheme according to their degree of development are open to question by workers. The placement of plants in such a scheme varies with different workers, most of whom are plant anatomists.

The idea of classifying plants with respect to whether or not they are highly developed does not seem to be in question; in fact, much agreement prevails. It is the intermediate details that are the subject of controversy. Thus, the ecological conditions which permit or inhibit the growth of certain plants in particular localities arise from competition, temperature, moisture, and the presence or absence of elements needed by certain plants and not by others.

The majority of weeds found in the eastern part of the United States and perhaps in other parts of the world are of a high order of development: for example, the Compositae, the Graminaceae, the Boraginaceae, and the Convolvulaceae.

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Plants of these families are hardy individuals and are not easily affected by abnormal conditions such as too much or too little of the salts used in commercial fertilizers. The authors believe that the grasses and members of the aster family often withstand ten times the osmotic concentrations that are tolerated by the mallows, geraniums, or clovers. In places where the sea has been blocked off and the land claimed for agriculture, or where too large quantities of toxic salts of copper, mercury, or boron have been used, grasses are among the first economic crops that may be planted.

It was observed that on the magnesium-deficient plots at the Massachusetts Station, certain weeds were not bothersome. Thus, *Portulaca oleracea* (common purslane or "pussley"), *Oxalis corniculata* (wood sorrel), *Equisetum* (horse tails), and *Stellaria media* (chickweed), which are not considered to be highly developed, were not found growing where magnesium was not applied. On the other hand, grasses and wild members of the aster family had to be continually eradicated from such plots.

Where man has had a part in making the roots, herbage, or seed more productive or the flowers more florid, he has brought about a change in the physiological needs of the plants. Wild plants the needs of which man has had no part in thus changing are always more reliable, therefore, than the domesticated plants for detecting deficiency symptoms. At the Massachusetts Station this year, for example, three types of corn were planted on magnesium-deficient soil. One of these showed no chlorosis, another only to a slight degree, and a third—a hybrid sweet corn—grew to a height of only about 2 feet and never acquired tassels or seed. Potatoes also seem to be entirely different from their ancestors. Though less well developed than corn, they show marked magnesium deficiencies at times.

It is worthy of note that in the presence of some diseases, plants on low-magnesium soils, regardless of the stage of evolutionary development, manifest disease symptoms before plants grown on soils to which magnesium has been applied. For example, asters which acquired yellows manifested the disease symptoms earlier on the low-magnesium area. This year and during one or more years in the past, the vines of potatoes affected with blight died on the low-magnesium plot before those on the plot to which magnesium had been applied. Sunflower plants seemed to suffer more from leaf rust when grown on magnesium-deficient soil. It has also been observed that blight on cucumbers due to downy mildew was more severe on the low-magnesium area than on the more normal area, and plant lice intensified magnesium deficiency of nasturtiums. This combination of maladies may at times confuse the observer by the rapidity with which the deficiency symptoms occur.

There are a few important exceptions to the idea of evolutionary development in relation to magnesium needs. One of these is hybridization or extreme selection. Another is the fact that a number of plants do not chlorose. Some of the roses show no chlorosis, and some species such as the blackberry, the strawberry, and the apple, only slight chlorosis. These crops, however, are greatly impaired in growth and vitality by the low-magnesium content of the soil.

Another member of the rose family, the domestic raspberry, by its chlorosis and slow growth seems to be an excellent indicator of low-magnesium content of soil.

Let us consider at random a few domestic plants that may suffer quickly from low-magnesium content in the soil. Among the lower orders of seed plants, the mallow family includes such economic plants as cotton, okra, and hibiscus. Among the roses are apple, strawberry, blackberry, raspberry, plums, peaches, and many plants used as ornamentals. This family, perhaps more than all others, may suffer need for more magnesium without obvious *pathological* symptoms. Among the saxifrages are the hydrangea, syringa, currant, and gooseberry. Among the Cruciferae are such members as cabbage, cauliflower, rape, turnip, mustard, and broccoli. Among the isolated species are the American elm, magnolia, papaw, barberry, geraniums, and mulberry.

As was previously mentioned, there are two or more exceptions to these interpretations: one of these is the Solanaceae, and a second is at least one species of the Cucurbitaceae. The deficiency symptoms of the species of the latter family—field pumpkins—never are in evidence until maturity and seem not to influence vigor or yield, but the leaves are chlorosed and the intervencinal tissue falls out just before they die naturally. This seems like an unusual behavior. The Cucurbitaceae and the Solanaceae are, however, rather highly developed.

There are factors other than the degree of evolutionary development of the plant which often determine the amount of chlorosis. Among these are age and the degree of storage of the ions within the plant. Thus, tubers, biennials or perennials, when planted for their second year (or in later years in the case of perennials), in a plot which is deficient in magnesium after growing in one which is not deficient, may show no deficiency for several years. Among such plants are the floral lilies, onions, strawberries, gladioli, peaches, iris, and others. Certain plants like the peach and the apple may show definite magnesium-deficiency symptoms when they are young but recover when their roots penetrate more deeply into the soil and find sufficient magnesium in the subsoil. There is ample evidence that magnesium serves a greater role during the infancy of the plant than during the approach of maturity.

This discussion does not intend to convey the idea that there may not be areas in this country so deficient in magnesium that all of the plant kingdom suffers, but in the Massachusetts plot the deficiency is limited to the lower orders. It is entirely possible that, in the geological past, plants did not use so abundantly the elements that are used by our present-day plants. It is probable that so far as plant use is concerned, magnesium is an older element than calcium or nitrogen.

There is reason to believe that the alluvial soils are likely to show a greater deficiency of magnesium than the glacial till soils, as indicated by symptoms on crops. The various soils of the Connecticut River Valley show the deficiency more commonly than the drumlin-like soils of the uplands. Soils formed by glacial lakes of materials from the uplands also may be deficient in this element. Successive washing of the soil and the advent of man's constant cultivation have

been agencies in the near-depletion of the magnesium ion. It is not at all beyond the realm of possibility that the ecological distribution of plants—plant families which differ on alluvial soil from those families found on soil deposited by the glacier—may be determined in part by the relative proportion of this ion in the soil.

The expansion of civilization has given rise to deficiencies in both plant and animal life. In certain instances it became necessary to live on deficient soils and deficient herbage, since little was known of these deficiencies on the virgin soils in the not too distant past. When leaves and branches of the forest and the grass of the fields remained in the environment where they grew and when manures were later added to the fields, there was no evidence that nature failed to take care of the plant's needs. Later, when man began to cultivate and to add commercial fertilizers, there was a possibility that certain ions needed in the propagation of plants might be lacking. The authors found from chemical analysis that plants low in the plant kingdom, by reason of their capacity to grow well under adverse conditions, needed magnesium more than they needed calcium. Why this is true is not too apparent, but it is known that lichens, mosses, and some bacteria grow on rock ledges, Fungi, sphagnum, club mosses, and bacteria are low in calcium content; in fact, the first three of these have a calcium content of less than 0.2 per cent. When the earth was solid rock, the first plants had to obtain their nutrients with great difficulty. W. H. MacIntire has found that magnesium in dolomite dissolves and is removed more rapidly than is calcium. It is not uncommon that heterogeneous rocks weather more rapidly than the more homogeneous ones. Magnesium is often a part of a rock containing numerous elements. On the other hand, calcium occurs naturally to some extent as calcium carbonate or sulfate. Thus, early plants adjusted themselves to a medium of growth higher in magnesium than in calcium.

Again it must be pointed out that not all members of a family are assumed to behave alike, and that once quantitative methods can be substituted for observations on this subject, the results will be more satisfactory.

#### SUMMARY AND CONCLUSIONS

Among the lower groups of cotyledonous plants the extremes of plant development, from low to high, are as follows:

1. Ranales—buttercup, clematis, anemone, hepatica, marsh marigold, columbine, larkspur, and peony
2. Magnoliaceae—tulip tree, flowering magnolia, cucumber tree
3. Anonaceae—the pawpaw
4. Others, only slightly higher—the mallows, poppies, elms, geraniums, mulberry, the Cruciferae family, of which there are many garden plants.

Among the highest in development are the following:

1. Ambrosia genus of the Compositae—ragweed
2. Asters and daisies
3. Campanulates, including the bellflower and the Venus looking-glass
4. Labiates, including the mints.

Among the lowest of the monocotyledonous plants is the alismales, including water plantain and arrowhead. The highest of this group are the families of orchids and, slightly lower, the grasses. The latter have great economic significance.

On the main line, representing graphically the development of seed plants, there seems little doubt that resistance to magnesium deficiency increases as one goes up. When all the side branches are included, all the lower branches representing the lower orders show the deficiency quickly, whereas none of the extremely high orders represented by the upper branches show the deficiency. There are two family members in the side branches which, the writers have observed, do not fit into the scheme. These are the Solanaceae and the Cucurbitaceae. Of these two families, the domesticated species shows the deficiency more quickly than does the wild species.

It is significant that the more highly developed seed plants, because of their greater sturdiness, are far more resistant to abnormal agencies such as disease conditions, extremes of temperature, and high or low concentrations of elements. Such plants probably represent a general situation rather than the need of a specific ion by a specific species.

In the course of the experiment described in this paper, thousands of plants were seeded directly in the field and thousands were transplanted. Many of these plants were lost by lack of germination, resistance to transplanting, and lack of adaptability to new environment. *But*, for every one of the higher orders lost, approximately *ten* of the lower orders were lost.



## MAGNESIUM-PHOSPHORUS RELATIONSHIPS IN PLANT NUTRITION<sup>1</sup>

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One of the functions ascribed to magnesium in plant nutrition is that of a carrier of the phosphorus used by the plant. If this is the case, one might expect to find some sort of positive correlation between the phosphorus and magnesium contents of plants or between the efficiency of phosphate fertilizers and the supply of available magnesium. The literature dealing with this field was reviewed recently very completely by Beeson (4, 6). To summarize, it may be said that the results of most of the past experiments reveal a positive correlation. In some of the experiments the method of investigation was such as to preclude definite conclusions.

Of particular interest to the fertilizer industry in this connection are some recent developments in the conditioning of superphosphate with magnesium silicates. Experiments in Russia (7) about 10 years ago showed that when 8 to 9.5 per cent of dunitite (a material consisting largely of olivine— $\text{Mg}_2\text{SiO}_4$ ) was added to ordinary and triple superphosphate for the purpose of neutralizing excess acidity and absorbing moisture so as to facilitate handling, a product was obtained that had superior plant growth promoting properties.

In an attempt to make the limited supply of superphosphate go further during the war, workers (1, 2, 3, 8) in New Zealand took up the Russian idea of adding a magnesium silicate. Since serpentine ( $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ ) was at hand, it was used after being ground so that somewhat more than 90 per cent passed a 100-mesh sieve. One part was mixed with three or four parts of superphosphate. It is reported that the serpentine causes extensive reversion of the phosphate with reduction of water solubility but not of citrate solubility. When the serpentine and superphosphate are mixed dry, the reaction is virtually complete in 2 weeks, but when they are mixed with about 5 per cent of water it takes only 4 days. During this time the free acid is neutralized and moisture is absorbed or fixed as water of crystallization so that the product no longer attacks bags and in addition handles and drills nicely.

As the result of extensive field trials, it was established that the so-called serpentine superphosphate is in all cases equal in value to the standard superphosphate and in many cases superior. In 1942, 31,000 tons of serpentine was thus used, and in 1943, 62,000 tons.

This work in Russia and New Zealand indicates that the magnesium, which is supplied as a silicate and made soluble through interaction with the superphos-

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phate, facilitates the use of the phosphate by the crops grown. In other words, the results support the idea that one of the functions of magnesium is to act as a carrier of phosphorus. Of course, it might be argued that the reverted phosphate, being less soluble, becomes less subject to fixation in difficultly available form in the soil, and thus remains more available for plant use. This contention is supported by the superior results obtained in some tests in this country where lime was mixed with the superphosphate before application. Here, however, the presence of magnesium in the lime may have had an influence.

In Germany (9, 10), basic slag containing about 6 per cent of  $MgO$  has in a number of cases given better crop yields than superphosphate, or superphosphate with lime, and this advantage is ascribed to the presence of the magnesium in the slag.

During the last 2 years, several experiments bearing on this subject have been carried on in Wisconsin, and a report of these follows.

#### FIELD EXPERIMENTS WITH PEAS

In 1945, a rather extensive lime and fertilizer field experiment was started on Carrington silt loam near Beaver Dam, Wisconsin, involving a 4-year rotation of peas, alfalfa, alfalfa, and sweet corn. The original pH of the soil was 5.3, and the levels of available phosphorus and potassium were 20 and 120 pounds per acre plow layer respectively.

The experiment involves 156 plots variously limed and fertilized to establish and maintain the pH and fertility levels given in table 1. In order to promote thorough incorporation of the lime and fertilizer with the soil, one half of these materials was applied before plowing and disced in, and the other half after plowing followed by discing.

The lime used was dolomitic, analyzing 50.6 per cent of calcium carbonate and 41 per cent magnesium carbonate. It was finely ground, so that 97.8 per cent and 72 per cent passed a 100-mesh and a 300-mesh sieve respectively. The phosphate and potash fertilizers used were 45 per cent and 60 per cent materials respectively.

One series of plots limed to pH 6.5 has not had the basic treatments of phosphate and potash fertilizers to raise the fertility to the definite levels given in table 1, but is receiving, on the acre basis, 800 pounds of 3-12-12 fertilizer for peas and a similar amount for corn. This fertilizer for some of the plots contains magnesium sulfate so as to supply the equivalent of 40 pounds per acre of  $MgO$ .

Chemical analyses of peas (Alaska variety) produced the first year following these treatments (four plots with and four without magnesium sulfate) showed average increases in contents of phosphorus and magnesium of approximately 8 per cent and 9 per cent respectively, indicating, if anything, a positive correlation between the contents of these two elements.

In 1946, however, the content of these two elements in the peas was precisely the same regardless of additions of magnesium sulfate. Without doubt, the magnesium in the dolomite following a lapse of one year from its addition to the

soil had become available to the plants, and hence any influence of the magnesium sulfate was completely masked. This is supported by the fact that the magnesium content of the peas from all of the plots was substantially higher than the previous year. This high content of magnesium was reflected in a uniformly

TABLE 1

*Influence of dolomitic lime and of phosphorus and potassium fertility levels on nitrogen and mineral content of peas (seed) at canning stage*

Peas grown on Carrington silt loam, experimental field, Canniff Farm, near Beaver Dam, Wisconsin, in 1916. Lime added and fertility levels established previous year

PLOT NO	POUNDS PER ACRE FLOW LAYLR AVAILABLE		POUNDS 0-20-20 AT SEEDING TIME*	pH OF SOIL	TONS DOLOMITIC LIME ADDED	PERCENTAGE CONTENT OF PTAS (DRY BASIS) OF ELEMENTS INDICATED					YIELD, POUNDS GREEN PEAS PER ACRE
	P	K				N	P	Mg	Ca	K	
2B3	20	120	None	5.3	0	3.91	.33	.189	.075	1.32	1509
2C6	20	120	None	(6.5)	3	4.07	.37	.195	.077	1.33	2052
2D6	20	120	None	(7.5)	6	4.08	.47	.206	.079	1.39	2376
2B6	20	120	200 W.S.	5.3	0	4.00	.36	.180	.073	1.40	2484
2C1	20	120	200 W.S.	(6.5)	3	4.12	.39	.201	.078	1.42	2412
2D4	20	120	200 W.S.	(7.5)	6	4.15	.44	.215	.072	1.42	2526
2B5	50	150	200 W.S.	5.3	0	4.04	.36	.176	.069	1.43	2855
2C4	50	150	200 W.S.	(6.5)	3	4.11	.40	.202	.083	1.45	2394
2D1	50	150	200 W.S.	(7.5)	6	4.18	.42	.206	.069	1.44	2741
2B1	75	200	200 W.S.	5.3	0	3.90	.38	.187	.078	1.45	2268
2C2	75	200	200 W.S.	(6.5)	3	4.18	.40	.210	.075	1.47	2473
2D3	75	200	200 W.S.	(7.5)	6	4.20	.47	.221	.082	1.44	2709
2B4	125	300	200 W.S.	5.3	0	4.04	.37	.181	.070	1.47	2233
2C5	125	300	200 W.S.	(6.5)	3	4.15	.43	.204	.075	1.50	2681
2D5	125	300	200 W.S.	(7.5)	6	4.14	.51	.217	.075	1.49	2555
2B2	125	300	200 Br.	5.3	0	4.02	.38	.186	.069	1.46	2052
2C3	125	300	200 Br.	(6.5)	3	4.13	.42	.206	.073	1.49	3078
2D2	125	300	200 Br.	(7.5)	6	4.17	.49	.214	.070	1.47	3402

\* W.S., with seed; Br., broadcast.

high phosphorus content, which averaged the same as that of the peas grown the previous year on soil treated with magnesium sulfate.

In another pea experiment started in 1946 on a field near Waupun, Wisconsin, fertilizer was applied both with and without magnesium sulfate. The field had previously received some lime (very likely dolomitic) but not nearly enough to neutralize the acidity. Analyses of the peas produced showed a slight but consistent increase in content of phosphorus and magnesium for those receiving magnesium sulfate.

The most extensive analytical data, obtained by the authors in 1946, bearing on this subject and involving peas (Alaska variety) grown on field plots are those

presented in table 1. These data make possible correlation studies between the phosphorus and magnesium contents of peas grown at three lime (dolomitic) levels and five phosphorus levels. The yields of peas per acre ranged from approximately 1,500 pounds on the check to slightly more than 3,000 pounds on the most highly fertilized and limed plots.

It will be noted first of all that without the addition of lime (magnesium), increasing phosphorus levels have increased the phosphorus content of the peas only very slightly, and the magnesium content not at all. In contrast to this, increasing lime (magnesium) levels have increased the phosphorus content consistently and nearly as much at the low phosphorus levels of the soil as at the high. The content of magnesium has been raised appreciably and consistently with increasing lime (magnesium) levels. Table 2 gives the averages of all of the analyses for each lime level.

TABLE 2

*Averages of all results in table 1 at each lime level, showing influence of dolomitic lime on nitrogen and mineral content of peas at canning stage*

TONS DOLOMITIC LIME ADDED	pH OF SOIL	PERCENTAGE CONTENT OF PEAS (DRY BASIS) OF ELEMENTS INDICATED				
		N	P	Mg	Ca	K
0	5.3	4.00	.36	.183	.072	1.42
3	(6.5)	4.13	.40	.203	.077	1.44
6	(7.5)	4.15	.47	.213	.075	1.44

These data lend strong support to the contention that a high phosphorus content of peas (seed) is correlated with a high magnesium content and a high level of available magnesium. This deduction in turn supports the theory that magnesium serves as a carrier of phosphorus within the plant. It hardly seems tenable to argue that the increased phosphorus content of the peas grown on the limed soil is due to promotion by the lime of a higher availability of the phosphorus, for then it would be expected that the increasing levels of available phosphorus which existed without lime should also have raised the phosphorus content of the peas more markedly than was the case.

It will be noted that the nitrogen content went up slightly with increasing lime levels but not with increasing available phosphorus levels of the soil. The potassium content rose somewhat with increasing supplies of this element in available form. The calcium content showed a tendency to drop with an increasing potassium content.

#### WATER CULTURE EXPERIMENT WITH PEAS

In order that the foregoing results obtained with the peas grown in the field experiment might be checked under more closely controlled conditions, peas (Alaska variety) were grown in water cultures. The culture vessels consisted of 1-gallon earthenware jars, into each of which 3 liters of the culture solution was

placed, leaving space at the top for introduction of a wire screen on which to support the plants and a layer of glass wool which served as a cover and as protection.

The nutrient solution in the cultures was aerated continuously and renewed twice weekly. It was compounded as follows with varying concentrations of phosphorus and magnesium:

Element	p.p.m. in solution	Salts used
P	10, 30, and 90	$\text{KH}_2\text{PO}_4$
Mg	1, 5, 25, and 100	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
K	190	$\text{KH}_2\text{PO}_4$ and $\text{K}_2\text{SO}_4$
Ca	163	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
N	135	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{NH}_4\text{NO}_3$
Fe	15	$\text{FeC}_6\text{H}_5\text{O}_7 \cdot 5\text{H}_2\text{O}$ (approx.)
Mn	1	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$
B	0.5	$\text{H}_3\text{BO}_3$
Cu	0.1	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$
Zn	0.4	$\text{ZnCl}_2$

TABLE 3

*Influence of varying magnesium and phosphorus contents of nutrient solutions on growth of peas and on their contents of these elements*

Mg IN NUTRIENT SOLUTION	10 P.P.M. P IN NUTRIENT SOLUTION				30 P.P.M. P IN NUTRIENT SOLUTION				90 P.P.M. P IN NUTRIENT SOLUTION			
	Yield		Content in seed		Yield		Content in seed		Yield		Content in seed	
	Seeds	Vines	P	Mg	Seeds	Vines	P	Mg	Seeds	Vines	P	Mg
	p.p.m. gm.	gm.	per cent	per cent	gm.	gm.	per cent	per cent	gm.	gm.	per cent	per cent
1	.5	8.5	.36	*	1.0	7.5	.36	*	1.0	7.5	.39	*
5	3.5	10.0	.39	.121	3.5	10.5	.42	.118	3.5	10.0	.46	.134
25	7.0	15.0	.41	.139	6.0	17.0	.42	.127	8.0	17.0	.48	.142
100	7.5	15.0	.43	.150	7.5	16.0	.46	.167	8.5	15.0	.53	.167

\* Sample weight insufficient for Mg analysis.

Twelve plants were grown per culture, and cultures were set up in duplicate. The peas supplied with 25 and 100 p.p.m. of magnesium made a good normal growth; those supplied with less soon developed characteristic magnesium-deficiency symptoms. After 6 weeks' growth, when the peas had reached the canning stage, the crop was harvested, dried, weighed, and analyzed for phosphorus and magnesium. The results are given in table 3.

It will be noted that with 25 and 100 p.p.m. of magnesium, yields of seed and vines did not vary much with the concentration of phosphorus, although they were perhaps slightly better with the highest concentration. This shows that available phosphorus could not have been a limiting factor, and any increase in phosphorus content of the peas that occurred with the higher concentrations of magnesium would have to be ascribed to some action of the magnesium. It will be noted that the phosphorus and also the magnesium contents rose appreciably and consistently with increasing concentrations of magnesium.

These results fully confirm those obtained in the field experiments and lend strong support to the theory that magnesium functions as a carrier of phosphorus. It is believed by the authors that analysis of the seeds of plants furnishes a more reliable test of this theory than analysis of vegetative tissue, since in the latter, magnesium functions in various capacities, and vegetative tissue is subject to wide variations in composition due to the influence of many complicating factors. Finally, it should be added that in a recent publication, Beeson, Lyon, and Barrentine (5) reported some results, obtained with tomato plants grown in nutrient solutions, which showed a higher content of phosphorus in the leaves at the higher concentrations of magnesium.

All of these results emphasize the great importance of an adequate supply of available magnesium in soils to promote efficient utilization of phosphorus. Recognition of this is of tremendous practical importance, because it points the way to the production of seed and forage of greater feeding value, and possibly better seed for planting purposes. Failure in many experiments to produce crops of higher phosphorus content through phosphate fertilization has undoubtedly been due to a lack of available magnesium. The supply of available magnesium in soils and the use of magnesium-containing materials deserve much increased attention.

#### SUMMARY

The relation of the supply of available magnesium to the phosphorus content of peas (seed) was investigated by means of field and nutrient culture tests in which the supplies of available magnesium and phosphorus were varied. Chemical analysis of the pea seeds revealed an appreciable and consistent increase in phosphorus content with increasing supplies of available magnesium. In fact, increasing supplies of available magnesium increased the phosphorus content of the peas much more than did increasing supplies of available phosphorus.

The results support the theory that magnesium functions as a carrier of phosphorus. They also indicate the need of giving increased attention to the supplies of available magnesium in soils in order that the phosphorus present may be used effectively and crops of the highest nutritive value produced. Failure in many cases in the past to obtain crops of higher phosphorus content through the addition of phosphate fertilizer may well have been due to a lack of available magnesium.

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# SOME FACTORS INFLUENCING THE AVAILABILITY OF MAGNESIUM IN SOIL AND THE MAGNESIUM CONTENT OF CERTAIN CROP PLANTS<sup>1</sup>

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Magnesium is the key metallic substance in chlorophyll; therefore, it is of importance to those interested in the growth and production of crop plants. The magnesium in the chlorophyll seems to occupy a position similar to that of the iron in hemoglobin, where the iron is loosely bound and is evidently the active agent in the carrying of oxygen. Magnesium is more abundant in the parts of plants that are concerned with the vital processes such as seed and foliage than in the roots and stems. Therefore, the total amount of magnesium in the soil and the amount available to plants under different conditions are of special importance to those who grow crops with a relatively high magnesium requirement.

Goldschmidt (18) has pointed out that important processes of physical and chemical segregation and concentration dominated the history of matter during geochemical evolution, according to the different properties of the electronic shells of the various elements. During the primordial stages of differentiation of the globe, the distribution of the various chemical elements was essentially controlled by their chemical affinity toward oxygen and sulfur and by their latent heat of vaporization. The free energy of oxidation of the electropositive elements can be used as a suitable measure of the chemical affinities of the various elements toward oxygen. The process of crystallization of magmas involves a sorting or selection of various atomic ions according to their size and with regard to their faculty for entering the crystal lattices or spacial network of the different minerals which crystallize from magmatic solutions. According to Goldschmidt, the possibility of large-scale isomorphous substitution in minerals from magmas will be limited to pairs of ions the radii of which agree within a tolerance of 10 to 15 per cent of the larger radius of the pair. Magnesium with a radius of 0.78 A. and ferrous iron with a radius of 0.83 A. freely replace each other in ionic crystals. Soils containing large quantities of iron usually contain a relatively large amount of magnesium. Since the ionic radii and the oxidation potentials of the elements are dominant factors in the association and distribution of nutrients, it follows that some consideration should be given to the properties of nutrients in relation to their distribution and availability to different plants.

Nature has provided plant cover for virtually all soil conditions where sufficient moisture is available; therefore, it is not logical to expect any single property of a nutrient to determine the intensity of its availability to all plants. There is apparently a selective absorption of certain combinations of nutrient ions similar

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to the association of ions comprising the fractional crystallization of silicate magmas. Data presented by Cooper and Blink (15) suggest that halicystis selectively absorbs Na and Mg, which are isoelectronic with neon; however, most plants seem selectively to absorb metallic ions with valence shell isoelectronic with argon (20, 31).

The amount of magnesium in most plants usually ranks third or fourth in the metallic nutrients. In humid regions where the amount of sodium in the soil solution is relatively low, magnesium ranks third. In subhumid to arid regions or where a large amount of sodium is present in the soil, the quantity of potas-

TABLE 1

*Normal electrode potentials relative to the normal hydrogen electrode and ionization potential in equivalent volts in various states of ionization of certain plant nutrients*

The sign of the potential is opposite the sign on the electrode

ELECTRODE REACTION OF ELEMENT	NORMAL ELECTRODE POTENTIAL	APPROXIMATE EQUIVALENT ENERGY IN VOLTS FOR REMOVAL OF VALENCE ELECTRONS			
		Removal of last bound electron		Removal of inmost common valence electron	
		Element	Equivalent volts	Element	Equivalent volts
	<i>volts</i>				
$K = K^+ + e$	+2.92	$K^+$	4.318	$K^+$	4.318
$Na = Na^+ + e$	+2.71	$Na^+$	5.120	$Na^+$	5.120
$Ca = Ca^{++} + 2e$	+2.50	$Al^+$	5.960	$Ca^{++}$	11.62
$Mg = Mg^{++} + 2e$	+1.55	$Ca^+$	6.09	$H^+$	13.52
$Al = Al^{+++} + 3e$	+1.28	$Mn^+$	7.41	$Mg^{++}$	14.96
$Mn = Mn^{++} + 2e$	+1.00	$Mg^+$	7.61	$Mn^{++}$	15.70
$Zn = Zn^{++} + 2e$	+0.76	$Cu^+$	7.68	$Fe^{++}$	16.16
$Fe = F^{++} + 2e$	+0.43	$Co^+$	7.81	$Co^{++}$	17.30
$Co = Co^{++} + 2e$	+0.29	$Fe^+$	7.83	$Zn^{++}$	17.89
$H = H^+ + e$	$\pm 0.00$	$Zn^+$	9.36	$Cu^{++}$	20.34
$Cu = Cu^{++} + 2e$	-0.34	$H^+$	13.52	* $Al^{+++}$	28.31

\* The volts required to remove second valence electron  $Al^{++} = 18.74$ .

sium, sodium, and calcium is greater than that of magnesium in many plants.

Since two or three strong metallic cations are selectively absorbed in preference to magnesium by certain plants, some of the chemical and physical properties of nutrients directly concerned with the nutrition of plants should be considered.

Some important properties of different nutrients are the strength of ions and their solubility. It is of special interest, therefore, to consider certain measures of ionic strength such as standard electrode potentials, ionization potentials, and the solubility of different nutrient compounds.

#### NORMAL ELECTRODE POTENTIALS OF CERTAIN NUTRIENT ELEMENTS

The normal electrode potentials reported by Kolthoff and Furman (25) and in the International Critical Tables (24) of certain nutrient elements included in table 1 are useful in predicting the relative availability and the absorption of

nutrient ions. The average chemical analysis of a large number of plants included in tables 3 and 4 shows a close correlation between the relative strength of ions and the amount of the nutrients in the plants. It is now generally recognized that there is very little correlation between the concentration of salts in the nutrient media and the absorption of ions. The relative strength of ions as measured by their normal electrode potentials is a measure of the intensity factor of energy rather than of the capacity or quantity factor. The relative strength of ions seems to be one of the most significant factors in the absorption and utilization of nutrients, yet these values have been given very little consideration in nutrition studies. Some of the fundamental problems in nutrition will probably not be solved until more general use is made of the known chemical and physical properties of nutrients.

#### IONIZATION POTENTIALS OF NUTRIENTS

The ionization potentials of nutrients in various states of ionization reported by Millikan and Bowen (29), Noyes and Beckman (30), and Latimer and Hildebrand (26) are included in table 1. It is interesting to note the order of ions in this grouping. The equivalent energy required for the removal of the last bound electron is shown in column four. This grouping gives little idea of the activity of ions other than such monovalent ions as K, Na, and H. The values in column six give a better idea of the relative activity of ions in their most common atomic ionic valence state. The atomic ionic series in this group, according to strength, is K, Na, Ca, H, and Mg. In this grouping the hydrogen ion ranks next to calcium in strength and would be likely to predominate over any ion below it in this series. This grouping is in agreement with the established order of activity of certain ions in the soil colloidal complexes.

#### SOLUBILITY OF NUTRIENT COMPOUNDS

The data in table 2, compiled from various solubility tables, are of interest in certain studies in nutrition. As the solubility values reported were determined under different temperature conditions, it is not possible to make close comparisons of the relative solubility of materials. There is a wide variation in the solubility of different nutrient compounds. Virtually all the potassium salts are soluble in water, as are the salts of other alkali metals such as sodium and rubidium. The ammonium salts are also soluble in water. There is a wide variability in the relative solubility of the other materials included in the table. It is important to note the low solubility of the carbonate, oxalate, hydroxide, and phosphate compounds of calcium and the other metals below calcium in this grouping.

#### INTENSITY OF REMOVAL OF CATIONS FROM SOILS BY ELECTRODIALYSIS

Cooper and Paden (10) have pointed out that there is a definite relation between the removal of cations from soils by electrodialysis and the relative strength of ions. In a soil fractional electrodialysis study, 56.00, 24.66, 17.49, and 11.98 per cent of added equivalent quantities of K, Na, Ca, and Mg were removed in

the first 2 hours. This clearly demonstrates the difference in intensity of the removal of ions from soils by electrodialysis.

#### COMPOSITION OF PLANTS

The mineral content of crops is important to those interested in the optimum conditions for plant growth. It is desirable, therefore, to consider some of the effects of different nutrients on plant growth. These nutrients play a significant part in plant growth as follows: (a) they serve as a structural, or integral, part of compounds, as carbon in organic compounds; (b) they are necessary for oxidation-reduction reactions in the plant at definite energy levels; (c) they determine the ionic balance in plants; (d) they influence the pH of the cell sap, buffer capacity, and the absorption of nutrients; and (e) they may mobilize or immobilize certain materials in the various plant tissues.

TABLE 2

*Solubility of certain nutrient compounds in grams of anhydride per 100 gm. cold-water solution*  
Temperature around 20° or zero centigrade as indicated\*

ION	HCO <sub>3</sub>	CO <sub>2</sub>	CaO <sub>4</sub>	OH	PO <sub>4</sub>	HPO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub>	SO <sub>4</sub>	NO <sub>3</sub>	Cl
K	22.4	112.0	33.0	97.0°	S.S.	V.S.	33.0	12.0	31.6	34.7
NH <sub>4</sub>	11.9°	100.0	4.0	42.0	.....	42.9°	22.7°	70.60°	118.3°	29.7°
Ca	....	0.0014	0.00067	0.185°	0.002	0.02	1.80	0.298	102.0°	59.5°
Mg	....	0.0106	0.07	0.0009	0.02	0.31	.....	26.0°	42.33	35.3
Mn†	....	0.0065	0.03	0.0002	.....	....	.....	52.0	426.4°	62.2
Zn	....	0.001	0.00079	0.00000026	i	i	i	86.5° <sup>90</sup>	327.3 <sup>40</sup>	432.0
Fe†	....	0.0067	0.022	0.00067	.....	....	.....	15.65	83.5	64.4
Co†	....	i	i	0.00032	i	....	.....	36.2	133.8°	45.07
Cu†	....	i	0.0025	i	i	i	i	14.3°	137.8°	70.6°

\* Many of the values in this table were taken from Handbook of Chemistry and Physics by C. D. Hodgman and H. N. Holmes, Chemical Rubber Publishing Co., 1941. S.S. = slightly soluble; V.S. = very soluble; i = insoluble.

† Divalent.

The chemical composition of hay and forage crops reported by Snider (33) is included in table 3. These data represent a very extensive study of the chemical composition of crop plants grown under different conditions. The metallic constituents are arranged in order of the normal oxidation-reduction potentials or the relative strength of ions. It is well established that there is a selective absorption of nutrient elements, and that the concentration of the material in the nutrient medium is not the major factor, under ordinary conditions, in determining the rate or intensity of absorption of most nutrient ions. Since the normal electrode potential is a measure of relative activity or the intensity factor of energy, consideration should be given to the relation of strength of ions to selective absorption by plants. As already pointed out by Cooper and Paden (10), there is a direct correlation between normal electrode potentials of elements and their removal from soil colloids in electrodialysis. The same general relation holds for the removal of metallic cations from plant tissue by electrodialysis (11).

There is a close correlation between the strength of ions and the mineral analysis of plants. The last line in table 3 expresses the amount of metallic nutrients

TABLE 3  
*Removal of nutrients in pounds per ton of hay and forage crops in Illinois*

HAY AND FORAGE CROPS	NUMBER OF SAMPLES	K	Ca	Mg	Mn	Fe	P	N	TOTAL ELEMENTS	PROTEIN
<i>Leguminous forage crops</i>										
Alfalfa.....	50	25.0	35.0	9.8	0.02	0.16	3.6	55.0	128.58	344
Red clover.....	50	26.0	29.4	9.2	0.10	0.28	3.2	47.4	115.58	296
Alsike.....	20	22.4	26.2	10.6	0.09	0.30	4.2	47.0	110.79	294
Lespedeza.....	50	18.9	17.0	5.7	0.14	0.20	2.9	40.4	85.24	252
Soybeans (pod stage)....	50	17.8	25.0	17.4	0.17	0.46	3.4	43.6	107.83	272
Sweet clover (full bloom)	7	19.4	42.0	13.4	....	....	3.0	34.4	112.20	215
Sweet clover (Oct.-Nov.).....	17	16.0	27.0	12.4	0.20	0.30	2.2	41.4	99.50	259
Sweet clover (April-May).....	30	32.0	32.8	11.4	....	....	6.0	69.0	151.20	431
Cowpeas.....	3	25.2	30.2	14.2	0.97	0.38	3.5	49.6	124.05	310
Average.....	277	22.5	29.4	11.6	0.24	0.30	3.5	47.5	115.00	297
Per cent of K.....	...	100.0	130.66	51.55	1.06	1.33	15.55	211.11	.....	...
<i>Nonleguminous forage crops</i>										
Kentucky bluegrass....	50	32.8	6.2	4.0	0.19	0.26	3.8	29.4	76.65	184
Timothy.....	50	31.4	5.6	3.6	0.14	0.16	3.0	19.6	63.50	122
Redtop.....	50	31.8	8.4	4.4	0.43	0.18	3.4	21.2	69.81	132
Orchard grass.....	30	38.0	5.4	4.2	0.56	0.16	3.6	19.4	71.32	121
Brome grass.....	50	44.3	8.0	3.0	0.24	0.12	3.4	29.8	88.86	186
Big bluestem.....	10	29.6	7.6	4.1	0.12	0.29	3.0	21.4	66.11	134
Cornstalks.....	50	23.0	9.8	8.4	0.28	0.36	1.8	14.8	58.44	92
Wheat straw.....	20	14.6	3.2	2.2	....	....	0.8	8.0	28.80	50
Oat straw.....	10	31.0	5.0	3.4	....	....	1.6	13.8	54.80	83
Average.....	320	30.7	6.6	4.1	0.28	0.22	2.7	19.7	64.25	123
Per cent of K.....	...	100.0	21.50	13.35	0.91	0.72	8.79	64.17	.....	...
Average legumes and nonlegumes.....	597	26.6	18.0	7.8	0.26	0.26	3.1	33.6	89.62	210
Per cent of K.....	...	100.0	67.67	29.32	0.98	0.98	11.65	126.31	.....	...

in plants in terms of percentage of K, the most abundant metallic constituent in most groups of plants. In the legume crops, however, there is more calcium than potassium and more iron than manganese. These data show that it is not possible to make a general classification of the order of intake of nutrients by

various plants. Some plants have the capacity to accumulate large quantities of certain nutrients, such as aluminum reported by Hutchinson (23) and Robinson and Edgington (32). The accumulation of some of the weaker ions is probably made possible through the formation of such insoluble compounds as oxalates and pectates.

The variation in the chemical analysis of alfalfa leaves grown on seven Michigan soil types as reported by Fonder (16) and Beeson (1) is shown in table 4.

TABLE 4

*Variations in the potassium, calcium, and magnesium content expressed as per cent of the leaves of alfalfa grown on seven Michigan soil types*

STAGE OF GROWTH	PER CENT OF PLANT			
	K	Ca	Mg	Total
May 8.....	2.80	1.293	0.256	4.349
May 22.....	1.83	1.677	0.267	3.774
June 7.....	1.50	2.547	0.295	4.342
July 2.....	1.71	3.065	0.356	5.131
Average.....	1.96	2.146	0.294	4.399
Per cent change May 8 to July 2...	-38.93	137.05	39.06	17.98
<i>Average for four harvest periods on each soil type</i>				
Plainfield loamy sand.....	2.90	1.648	0.284	4.832
Coloma loamy sand.....	2.24	1.880	0.263	4.383
Hillside sandy loam.....	1.91	2.425	0.260	4.595
Fox sandy loam.....	1.57	2.609	0.387	4.566
Conover loam.....	1.57	2.298	0.336	4.204
Brookston loam.....	1.90	1.932	0.242	4.074
Miami silt loam.....	1.55	2.036	0.277	3.863
Average.....	1.95	2.118	0.293	4.360
Maximum of variation from lowest value.....	87.10	58.31	59.92	25.08

The potassium and calcium contents of the leaves varied widely and showed a more or less negative correlation over the sampling period. The chemical composition of the alfalfa at different stages of growth shows some significant relationships. Potassium decreased with the season from 2.80 per cent on May 8 to 1.71 per cent on July 2, while calcium increased from 1.293 per cent to 3.065 per cent. The magnesium content of the leaves was higher on June 7 and July 2 than it was earlier. The content of magnesium is in agreement with the intensity of its removal from plant tissue reported by Cooper, Paden, and Smith (11), who showed that the amount of magnesium removed by electrodialysis was relatively low until the stronger ions were removed. The quantity of magnesium in the leaves remained relatively low as long as the potassium level in the plant was

relatively high. The lack of magnesium in early spring grass may result in so-called grass tetany in animals grazing young grass on soils low in available magnesium or where the soil solution contains a high concentration of the

TABLE 5

*Average percentage of principal chemical elements in the dry matter of some important groups of crop plants*

CROP	K	Ca	Mg	P	S	Cl	N	TOTAL
Cotton fiber.....	0.59	0.13	0.09	.05	.05	....	....	0.91
seed.....	1.20	0.15	0.35	.75	.26	....	3.96	6.67
plant.....	0.91	2.17	0.69	.23	.26	0.68	1.73	6.67
Tobacco leaves.....	2.20	2.84	0.46	.28	.54	0.60	4.00	10.92
stems.....	3.11	0.54	0.23	.26	.30	....	3.25	7.69
Potato tubers.....	2.28	0.05	0.13	.25	.12	0.29	1.67	4.79
tops.....	1.62	4.12	1.15	.26	.68	2.25	....	10.08
Tomato fruit.....	5.24	0.29	0.29	.51	...	....	4.51	10.84
vines.....	3.68	3.48	0.44	.32	.28	....	1.80	10.00
Sweet potato roots.....	1.21	0.08	0.16	.12	.12	0.06	2.63	4.38
Buckwheat hay.....	2.88	2.62	0.60	.54	...	....	0.89	7.53
Sugar cane stalks.....	0.56	0.07	0.06	.07	.06	0.21	0.92	1.95
leaves.....	1.10	0.54	0.40	.13	.13	0.29	0.28	2.87
Average.....	2.04	1.31	0.39	.29	.25	0.63	2.33	6.56
Average cereal grains.....	0.48	0.07	0.16	.38	.17	0.09	2.01	3.36
Average fodder straw.....	1.46	0.55	0.37	.10	.17	0.41	0.76	3.82
Average grass hays.....	2.09	0.57	0.24	.26	.12	0.62	1.36	5.26
Average legume seed.....	1.50	0.16	0.22	.57	.21	0.06	4.52	7.24
Average legume hays.....	2.05	1.30	0.32	.26	.27	0.60	2.57	7.37
Average roots and tubers.....	2.11	0.49	0.17	.28	.18	0.59	1.88	5.70
Average roots, tubers, tops....	3.12	2.24	0.65	.29	.45	2.35	3.90	13.00
Average leafy vegetables.....	4.37	1.24	0.27	.62	.85	0.96	4.35	12.66
Grand average.....	2.14	0.88	0.31	.34	.30	0.70	2.63	7.22
Per cent of K.....	100	41	14	16	14	33	123	337

stronger cations which may limit the absorption of the weaker magnesium ion by certain plants.

The average chemical composition of dry matter of a certain group of crops is shown in table 5. Most of these analyses were taken from the comprehensive study by Beeson (1) on the mineral composition of crops and reported in tables of crop composition. The composition of the tomato plant was reported by Hester (19). The data in this table indicate very definitely the correlation between the relative strength of ions and the composition of the crops. The

last line in the table shows the content of the materials expressed in terms of percentage of potassium. The calcium is 41 per cent and the magnesium 14 per cent of the potassium content of the plants.

There is a wide variation in the chemical composition of different plants. It is observed that certain plants are high in magnesium as compared with others. The entire cotton plant, tobacco leaves, potato tops, toamto tops, buckwheat plant, and sugar cane leaves are all relatively high in magnesium, and these crops require an adequate supply of available magnesium for optimum growth. These are among the crops showing the greatest response to magnesium added in fertilizers.

#### CARBONACEOUS AND PROTEINACEOUS PLANTS

Attention might be directed to the relatively small amount of calcium in the carbonaceous parts of plants such as seeds, roots, and tubers, and also to the fact that the amount of magnesium in seeds and tubers is nearly always greater than the amount of calcium.

The data in table 2 giving the solubility of different nutrient compounds may be of value in considering the carbonaceous and proteinaceous crops. It is generally accepted that production of carbonaceous plants is associated with a relatively large supply of available potassium. Since the production of carbonaceous material is the result of carbon dioxide assimilation, the solubility of the bicarbonates and the carbonates of potassium and ammonium as compared with the solubility of calcium carbonate might be of interest. It is not probable that a relatively large quantity of calcium bicarbonate would exist in any system in plants, because the conditions would very likely be favorable for the formation of calcium carbonate or other relatively insoluble calcium compounds. The data in table 2 suggest that it may not be possible to maintain an ample supply of carbon dioxide for maximum assimilation when excessive amounts of calcium are present within the plant, as insoluble calcium carbonate may be formed. In the presence of relatively large quantities of calcium, the nitrate and chloride are the only common nutrient anions that would be readily soluble in combination with calcium, and therefore, the synthesis of proteins might be relatively greater than the synthesis of carbohydrates where a limited supply of carbon dioxide is available. The relative quantities of carbon dioxide and nitrogen available to plants may determine the differential in the synthesis of carbonaceous or proteinaceous materials, depending upon the relative quantities of anions of these nutrients available for photosynthetic reactions. It is observed that many of the plants or tissues that are high in calcium are also high in chlorine. This relation might be expected, as the nitrate and chloride are the only common nutrient anions that would maintain a large supply of soluble calcium in the nutrient medium. Oxalates and pectates tend to precipitate the calcium and immobilize it in the plant. Magnesium carbonate is 10 times as soluble as calcium carbonate, and magnesium hydrogen phosphate is about 15 times as soluble as the calcium hydrogen phosphate.

The accumulation of magnesium and phosphorus in the seed and other storage

magnesium and phosphorus in reproduction and growth. This relationship suggests the necessity of an adequate supply of magnesium for the efficient utilization of phosphorus by plants. Plants have apparently developed some mechanism for excluding excessive quantities of calcium from seed and other storage tissues concerned with reproduction. It is probable that magnesium phosphate is the most stable phosphate compound that could be assimilated by the energy available to most seedling plants. The quality of energy resulting from respiration and oxidation processes would not be sufficient to assimilate phosphorus readily in as stable a compound as calcium hydrogen phosphate. The energy values involved in such reactions have been presented by Cooper *et al.* (8, 11) for certain nutrient compounds. It is noted from the free energy decrease values (8, 9, 10) calculated from normal electrode potentials and the discharge potential of phosphoric acid that the energy required for the decomposition of calcium hydrogen phosphate is 4.20 equivalent volts. This is equivalent to 2939 Å., or the shorter ultraviolet wave in sunlight; whereas the corresponding energy required for the decomposition of magnesium hydrogen phosphate is 3.25 volts, equivalent to 3798 Å., or the longer ultraviolet wave length of sunlight. The quality of the energy from respiration and oxidation processes of the stored organic constituents in seeds would probably be high enough for the assimilation of magnesium hydrogen phosphate, but not for the efficient assimilation of calcium hydrogen phosphate. Seeds and reproductive tissue are usually relatively high in magnesium and phosphorus. The partial exclusion or the limiting of the quantity of calcium in seeds and other tissues concerned with reproduction may be effective in supplying the seedling plant with a portion of the phosphorus needed for growth in less stable state than calcium hydrogen phosphate. It has been said that an abundance of potassium ions is required for the production of carbonaceous crops. The solubility values included in table 2 might suggest that the availability of the carbonate ions is the most important factor in determining the production of carbonaceous materials. Other ions of the alkali metals such as rubidium and sodium, and also the ammonium ion in some cases, may be about as effective as potassium in maintaining an adequate supply of available carbonate ions. The low solubility of calcium carbonate and other nutrient salts of calcium, with the exception of nitrate and chloride, may be the determining factor in the production of proteinaceous materials in the presence of a large amount of calcium.

Certain of the lower forms of plant life have the capacity to utilize atmospheric nitrogen. All higher forms of plants have lost this capacity, but they have developed a more important function, the ability to synthesize carbonaceous organic materials, which requires a higher energy level than does the synthesis of proteinaceous materials. The production of lignin, which allows expansion of plants to a great size and increases surface areas that are capable of photosynthesis, was one of the great advances in the evolution of plants.

Since a higher quality of light energy is required for the synthesis of carbonaceous materials than for the synthesis of proteinaceous materials, this may have been one of the important factors influencing the direction of the evolution of plants.



As magnesium is the strongest metallic nutrient that can be readily assimilated in the presence of the relatively energy-stable anions such as phosphates and carbonates, an adequate supply of available magnesium will be necessary if plants are to make the most efficient use of the stronger anions in photosynthesis. The efficient assimilation of calcium by many plants will be favored by having some of the nutrient calcium available in combination with weaker anions or anions less stable to light energy than are carbonates and phosphates.

#### MAGNESIUM IN FERTILIZER

As the availability of magnesium to plants is determined by a number of factors, it is not always possible to know under what conditions it is advisable to add magnesium to the fertilizer. Deficiencies of magnesium in plants may be due to a number of conditions such as insufficient supply in the virgin soil, insufficient rate of solubility, enhanced leaching through additions of anions forming soluble magnesium compounds, and insufficient rate of absorption due to selective absorption of the stronger nutrient cations such as K, Na, Ca, or  $\text{NH}_4$ .

Soil areas in which the supply of magnesium is inadequate are usually associated with regions of relatively heavy precipitation and leaching. Light sandy loams in the humid areas are most likely to be deficient in magnesium. Such soils usually have a favorable physical condition and when heavily fertilized produce a high yield of many crops, particularly vegetables. Heavy applications of fertilizer add large quantities of sulfates, chlorides, and sometimes nitrates to the soil. These anions form soluble salts with magnesium and thus favor the leaching of magnesium from the soil. The data in table 2 show that the solubility in grams of anhydride per 100 gm. of cold water is 26.0°, 35.3, 42.33 for magnesium sulfate, magnesium chloride, and magnesium nitrate, respectively. Bower and Turk (4) have reported that there may be a deficiency of available calcium and magnesium in alkali soils with high content of sodium. Since the soil they worked with contained a high content of  $\text{CO}_3$  and  $\text{HCO}_3$  ions, it is probable that conditions were favorable for the formation of relatively insoluble calcium and magnesium carbonates, which may result in a relatively low availability of these nutrients to plants under such soil conditions.

The mineral composition of a wide variety of crops, as shown in tables 3, 4, 5, and 6, definitely suggests that there is a selective absorption and utilization of stronger nutrient ions. The selection of ions by many plants can be correlated with the intensity factor of energy as measured by normal electrode potentials of certain metallic nutrients included in table 1. Since the intensity factor of 1.55 volts for magnesium is far below the normal electrode potentials of the stronger nutrient ions such as K, Na, and Ca (2.92, 2.70, and 2.50 volts, respectively), it is logical to expect that the stronger ions would be selectively absorbed by most plants. Evidence for such selective absorption of nutrients has been presented by Beeson (1, 2), Brooks (3), Carolus (5), Chapman (6), Collender (7), Cooper *et al.* (8, 9, 12, 13, 14), Cooper and Bink (15), Fonder (16), Garner (17), Hoagland *et al.* (20, 21, 22), Marshall (28), and Osterhaut (31). It seems that the most satisfactory way to study the conditions influencing the selective absorption of

nutrients is first to consider the properties of nutrient ions which would determine selective absorption in a wide variety of plants, and then to consider the characteristics of certain plants which may modify or counteract the inherent characteristics of certain ions which influence the rate or intensity of ion absorption by plants. As already pointed out, Goldschmidt (18) has drawn attention to the fact that the segregation and combination of elements into compounds in nature is correlated with such characteristics as radii of ions and the free energy of oxidation of electropositive elements. He has also shown that the associations of different elements in soil minerals may be reflected by the ash analysis of the plants grown on the soil.

TABLE 6

*Approximate amounts of important plant nutrients in dry matter of certain crops*

CROP	POUNDS PER ACRE IN SINGLE CROP				
	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	MgO
Cotton plant	90.0	30.3	53.8	60.2	26.0
500 pounds lint	1.0	0.6	3.2	0.8	0.7
1000 pounds seed	37.0	14.5	12.2	1.8	4.9
3000 pounds stalks	52.0	15.2	38.4	57.6	20.4
Tobacco, 1000 pounds leaves (flue-cured)	40.0	6.4	26.5	39.8	9.2
Cereal grains	26.0	12.0	7.0	2.0	4.0
Stover and straws	17.0	6.0	29.0	7.0	5.0
Grass hays	30.0	11.8	45.0	16.5	8.4
Legume hays	86.0	18.0	66.0	49.0	16.0
Roots and tubers	35.0	18.0	72.0	12.0	7.0
Leafy vegetables	38.0	16.0	66.0	33.0	8.0
Average for all crops.....	45.25	14.81	45.66	27.44	10.45
Per cent of K <sub>2</sub> O.....	99	32	100	60	23

Attention has already been directed to the fact that nature has provided plant cover for virtually every normal soil condition where sufficient moisture is available. It therefore appears that plants have acquired particular mechanisms for absorption and assimilation, depending upon the specific combinations of nutrients in the soil complex. The net result is a differential in the selective absorption of specific groups of nutrient ions with valence shells isoelectronic with such inert gases as neon, argon, or krypton, as data presented by Cooper and Blink (15) might suggest.

The principal chemical elements in the dry matter of some important groups of crop plants, included in tables 5 and 6, show interesting relationships. The fact that such materials as potato tops, cotton plants, buckwheat, tobacco leaves, and sugar cane leaves are relatively high in magnesium and that these crops are usually relatively high in carbonaceous compounds would indicate that magnesium may be closely associated with the assimilation of the carbonate ion.

The relatively low calcium content of seeds, tubers, and other highly carbonaceous materials suggests that some exclusion mechanism must be operating to prevent the accumulation of large quantities of calcium in seed or other tissue concerned with germination and growth of seedlings or young plants. The magnesium content of seed and certain other reproductive tissue very often exceeds the calcium content. There seems to be a positive correlation between magnesium and phosphorus contents of seeds. These data suggest that magnesium phosphate is the most stable phosphate that could be readily synthesized by the quality of energy available from respiration and oxidation processes in stored organic materials determining seedling growth. If large quantities of calcium were present in the seed, most of the phosphorus would tend to form the very energy-stable calcium phosphate, and the quality of the energy from respiration and oxidation necessary for germination and seedling growth would not be adequate for the efficient assimilation of phosphorus in the stable calcium phosphate form.

To conform with fertilizer terminology, the metallic nutrients are reported in our table 6 as oxides rather than as elements. It is often possible, however, to present the relative requirement for the different nutrients more clearly by expressing chemical composition in terms of elements.

A ton of dolomitic limestone broadcast per acre may supply the magnesium requirement of most crops for several years. As pointed out by MacIntire (27), the addition of calcitic limestone may aggravate magnesium deficiency of plants in certain soils. The use of dolomite in the production of nonacid-forming complete fertilizers will usually meet the annual requirement of magnesium for most crops, particularly those with a long growing season.

For rapid-growing short-season crops with a relatively high magnesium requirement, such as potatoes, tobacco, cotton, and certain leafy vegetables (table 5), it is usually desirable to add soluble magnesium compounds to the soils. An annual application of the equivalent of 20 to 30 pounds of magnesium oxide per acre in soluble magnesium salts is usually sufficient to supply the annual magnesium requirement of most crops. In humid regions, more frequent applications may be desirable, as the soluble magnesium salts may be readily leached from the soils.

#### SUMMARY

Magnesium is a constituent of chlorophyll and is apparently an active agent in the synthesis of carbonaceous materials from carbon dioxide.

The distribution and the availability of magnesium in soils are influenced by the segregation and concentration during the geochemical evolution of the globe. Important properties determining the distribution are the characteristics of the valence electronic shells and the free energy of oxidation and the radii of ions capable of readily entering into particular crystalline structures of soil minerals.

Since there is plant cover for virtually every normal soil where sufficient water is available, it is logical to assume that plants adapted to the different combinations of minerals will possess a differential in their absorption characteristics

which would enable some types of plants to grow successfully on soils with various combinations of nutrient materials.

Since the characteristics of the valence electron shells influence the activity of ions, those interested in the mineral nutrition of plants should give careful consideration to some of the well-established measures of the intensity factor of energy determining the relative activity of ions such as normal electrode potentials and ionization potentials of nutrient materials.

The ionization potentials present an ion series which may be helpful in predicting the release from soil colloids and the availability of atomic ions in soil complexes. This series suggests that the intensity of removal of atomic ions probably decreases in the following order: K, Na, Ca, H, Mg, Mn, and Fe.

Chemical analyses of a large number of plants grown over a wide range of conditions show that there is a very close correlation between the normal electrode potential, which is a measure of ion activity, and the mineral content of plants. These data may be considered as illustrating the general tendency for plants to absorb ions selectively according to relative strength rather than the relative concentration of ions in the nutrient medium.

The many deviations from the average chemical analysis presented suggest that the particular characteristics of certain plants may result in a differential in the selective absorption of combinations of nutrient ions whereby the plants become adapted to certain environmental conditions. In order to determine the factors affecting the selective absorption of nutrients, it will probably be necessary to consider properties of the ions in relation to the particular absorption characteristics of various groups of plants.

The partial exclusion or limiting of the strong calcium ion in seeds, tubers, roots, and other tissues concerned with reproduction suggests that plants possess some exclusion mechanism which prevents the accumulation of large quantities of certain strong ions which might depress seedling plant growth.

The relatively high content of magnesium and phosphorus in seeds suggests that magnesium may be the strongest cation which could be utilized in combination with phosphorus and give sufficient assimilation of phosphorus in the seed for normal growth of seedling plants. The quality of free energy decrease in the respiration and oxidation processes of the stored organic materials in seed would not be high enough for ready assimilation of phosphorus in a compound as stable as calcium hydrogen phosphate, which would require energy equivalent to the shorter ultraviolet wave length in sunlight. The quality of the free energy decrease in respiration and oxidation processes of organic compounds in seeds would very probably be as high as the discharge potential of magnesium hydrogen phosphate, which is equivalent to the longer ultraviolet wave in sunlight.

The production of highly carbonaceous plants has been associated with an abundant supply of potassium; and the production of proteinaceous materials, with a relatively large quantity of calcium in the nutrient complexes. The relative quantities of carbon dioxide and nitrogen available to plants may determine the differential in the synthesis of carbonaceous and proteinaceous

materials, depending upon the relative quantities of these materials available for photosynthetic reactions.

Since most plants selectively absorb the stronger nutrient, the magnesium content usually ranks third or fourth in quantity of metallic nutrients in plants. The stronger nutrient ions in the nutrient complex may definitely influence the solubility as well as the absorption of the relatively weaker magnesium ion.

In the metallic content of plants in humid climates, magnesium is exceeded only by potassium and calcium, which suggests that magnesium may be the next metallic nutrient that should be generally included in mixed fertilizer where heavy applications of fertilizers are common and relatively heavy yields of vegetative crops are expected. It is very probable that a deficiency of magnesium available to plants is a limiting factor in crop yields on many humid soils.

Crops containing a relatively large quantity of magnesium, such as potatoes, cotton, tobacco, tomatoes, and other vegetables, often give a marked response, as indicated by yields, to applications of magnesium in mixed fertilizers. The addition of large quantities of sulfates, chlorides, or nitrates will increase the solubility of magnesium in the soil and result in a heavy loss of magnesium through leaching in regions with high rainfall.

A broadcast application of dolomitic limestone may supply the magnesium requirement for a number of years. In the production of high-yielding crops with a short growing season such as tobacco, cotton, potatoes, and certain vegetables, the addition of the equivalent of 20 to 30 pounds per acre of magnesium oxide in soluble magnesium salts will usually satisfy the annual magnesium requirement on most soils.

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# MAGNESIUM IN CITRUS FERTILIZATION IN FLORIDA

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The magnesium requirement of plants is well known, and the use of magnesium as a fertilizer constituent is not new. Its general use in large areas, however, has come about only in recent years, mainly because the well-established belief that nitrogen, phosphorus, and potash constituted a complete fertilizer induced considerable resistance to the idea that other elements might play a part in the fertilizer picture. Much of the earlier work on fertilizers apparently was done on soils in which magnesium, copper, zinc, and other of the so-called "minor elements" were present in adequate amounts or to which sufficient amounts of these elements were supplied as impurities in the fertilizer materials used.

Some 50 years of experimental work on fertilizers in Florida and particularly on citrus was based on the presumption that only nitrogen, phosphorus, and potash were necessary, and the fact that materials being used in compounding the fertilizers contained other elements of value was generally overlooked. Bone meal, low-grade sulfate of potash, kainit, and wood ashes were favored materials; the fact that the outstanding results obtained by their use were due primarily to magnesium was unrecognized until recently. Not only were magnesium-containing materials favored in making fertilizer mixtures, but many of the companies also offered soil-corrective mixtures which contained wood ashes, hydrated dolomite, and other magnesium-bearing materials. Thus, the value of magnesium was recognized indirectly long before its use was rationalized. Exaggerated ideas as to the value and effects of potash developed, and many of these corrective mixtures contained potash materials that were supposed to accomplish results which we now know were due, not to the potassium in the mixture, but to the magnesium incidentally included. It may be said, therefore, that it is not the use of magnesium in citrus fertilization in Florida that is new, but only the understanding of its importance and its rationalization as an integral part of the fertilizer recommendations. The widespread use of magnesium as a recognized constituent of citrus fertilizers dates only from the middle thirties, but its use as an impurity in bone meal, potash, and wood ashes goes back to the beginnings of citrus fertilization in Florida when these materials were all part and parcel of the fertilizer program. Peculiarly enough, it was the introduction of new and purer materials that operated to force the recognition of magnesium.

## MAGNESIUM DEFICIENCY OF FLORIDA SOILS

Magnesium has always been deficient in the sandy soils of Florida and in many of the calcareous soils also. Some of the soils first used for citrus were higher in magnesium than are those commonly used today. This, together with the widespread use of magnesium-bearing fertilizer materials, produced excellent citrus. The soils planted in later years were deficient in magnesium in the



virgin state, and this deficiency combined with the gradual elimination of the magnesium-bearing materials brought on a general state of deficiency in the twenties and thirties which had a terrific impact on the production of citrus in Florida. In 1937 and 1938, Peech (8)<sup>1</sup> found that in the virgin state the ordinary Norfolk light sand which supported either pines or scrub oak commonly had about 10 pounds of exchangeable plus soluble magnesium per acre 6 inches and frequently had less; moreover, the total magnesium in such soils was also extremely low. Grove soils had a somewhat higher magnesium content than the virgin soils, because growers had been using bone meal and potash materials bearing some magnesium, plus some dolomite and magnesium sulfate. As the use of the latter two materials was new, however, the grove soils usually contained far too little magnesium to prevent the development of magnesium deficiency. Such light soils should contain about 80 pounds of exchangeable and soluble magnesium per acre 6 inches, whereas grove soils commonly contained less than 50. The magnesium content of the better sands was somewhat higher, but this was offset in a considerable degree by the higher calcium content, which as will be pointed out later, tends to offset the absorption of magnesium.

The calcareous soils in the coastal regions usually show a higher content of magnesium than do the sandy soils, but this is largely offset by the extremely high exchangeable and soluble calcium. As a result, magnesium is commonly deficient even on these soils and must be added in the fertilizer program. It was found that for citrus, in general, the ratio of exchangeable calcium to exchangeable magnesium ought to be within the range of 5/1 to 8/1, whereas the calcareous soils commonly have a ratio of 10/1 or 12/1, and some have a much higher ratio. Scarcely any grove soils in Florida have an adequate supply of available magnesium for citrus. In table 1, compiled from data by Peech (8), are given a few analyses of Norfolk soils, in which the virgin soil is compared with the soil in the adjacent grove, and also the maxima, minima, and averages for 55 samples taken from groves. In this latter group the average exchangeable plus soluble magnesium content was 39 pounds per acre 6 inches. Since the Norfolk is by far the most widely used soil series at present, it is evident that magnesium has indeed been deficient in grove soils.

Magnesium deficiency of citrus is not limited to Florida by any means. Probably the first report on the deficiency was from Brazil by Avena-Sacca in 1912. It has been reported from Australia and undoubtedly from other areas and observed by the writer in Jamaica, Trinidad, and Argentina.

As a basis for judging the magnesium requirements of citrus it may be said that the foliage contains only about two thirds as much phosphorus as magnesium and the fruit about three fourths as much magnesium as phosphorus [see Fudge (4, 6)]. Thus the magnesium requirements are at least equal in importance to the phosphorus requirements. Magnesium can hardly be classed as a minor element, therefore, but rather must be grouped with the so-called major elements. Since the soils used for citrus in Florida are about equally deficient in the two

<sup>1</sup> Only papers of particular interest are listed in this paper, since extensive bibliographies already have been published (see references 1 and 3).

elements, it is easy to see that the heavy applications of phosphorus used in the past, without additions of magnesium, were illogical.

#### MAGNESIUM-DEFICIENCY SYMPTOMS

The symptoms of magnesium deficiency in citrus have been described in detail by Camp and Fudge (1) and by several others but will be briefly reviewed here together with a discussion of more or less corollary troubles.

Trees deficient in magnesium and carrying a crop of fruit show a yellowing of the leaves during the late summer and early autumn. These yellow leaves start to fall once the magnesium is thoroughly depleted. Following drouth damage or cold injury in the autumn or winter, the leaf fall may be very rapid. As a result, the fruit is left exposed on defoliated twigs and may be injured by sunburn. A much more important factor is a marked reduction in fruit growth and in the development of sugar and vitamins, because there are no leaves to supply the necessary materials. This results in undersized fruit with low food value and markedly poor taste. Defoliated twigs commonly become infected by various fungi and they die back, necessitating heavy pruning after the crop is picked. There is a concordant reduction in the active root system and this may tend to reduce the intake of other elements and intensify other deficiencies. As previously reported by Camp (3), zinc deficiency is a common concomitant of such root damage, whether it be due to magnesium deficiency or other causes. It was not uncommon in the earlier days to find trees suffering acutely from magnesium deficiency and also showing marked deficiencies of both zinc and copper on soils fairly adequately supplied with the latter two elements. When such trees were supplied with adequate amounts of magnesium, most of the symptoms of the other deficiencies disappeared. Fudge was able to confirm, by leaf analyses, the increased absorption of copper by improved root systems following correction of magnesium deficiency.

Another result of magnesium deficiency thoroughly discussed by Fudge (4) is alternation in production, which is particularly apparent in the very seedy varieties but which holds in some degree for all varieties. This is brought about primarily by the fact that the acutely deficient trees lose so much young wood and foliage in the year of heavy cropping and put on so little additional growth during the spring and summer that after the crop has been removed and the tree pruned little wood of recent origin is left. It is this type of wood which produces bloom during the following spring. The net result is that the tree produces vegetative growth from the older wood the year following a heavy crop but produces little or no fruit. It should be mentioned, however, that this alternation is not strictly a tree function but, rather, is localized in the parts of the tree bearing a heavy crop. If one large limb on an otherwise heavy-bearing tree has little or no fruit, it may grow normally during the season and in turn produce a crop the following year. Thus, while magnesium is apparently transferred fairly readily from one twig without fruit to an adjacent twig with fruit, it is not transferred to any great degree from one sizeable limb to another. The exact details of the sizes and distances involved have not been

TABLE 1

*Analyses of some typical Norfolk soils before general use of magnesium and other secondaries, showing virgin soil analyses and comparable soils in groves together with maxima, minima, and averages for 55 grove samples*  
 Compiled from data by Peech (8)

SOIL TYPE	GROVE NO.†	SAMPLE NO.	DEPTH	pH	BASE SATURA- TION	EX- CHANGE CAPAC- ITY	EXCHANGEABLE BASES†								TOTAL N	ORGAN- IC MAT- TER	RATIO EXCHANGE CAPACITY % OR- GANIC MATTER	
							Ca	Mg	K	Mn	Zn	Cu	Acid- Soluble P	Water- Soluble P				
																		lbs.
Norfolk sand	2V	294	0-5	5.21	11.5	1.51	56	5	11	0.4	0.32	0.06	0	1	4	0.021	1.32	1.15
		295	5-18	5.31	10.8	0.60	13	.5	10	0.1	0.16	0.06	0	0	0	0.008	0.60	1.00
Norfolk sand	2	292	0-5	6.25	64.0	1.41	290	37	21	0.0	0.16	0.12	160	7	2	0.022	0.93	1.52
		293	5-18	4.96	13.5	0.80	28	5	13	0.0	0.16	0.06	32	2	0	0.008	0.63	1.27
Norfolk fine sand	19V	194	0-6	4.84	10.5	2.02	61	8	19	2.7	0.48	0.04	13	3	0	0.019	0.93	2.17
		195	6-18	5.41	9.0	0.89	20	3	13	0.8	0.16	0.04	22	1	0	0.007	0.41	2.17
Norfolk fine sand	19	192	0-8	5.09	37.5	2.13	280	11	38	3.6	0.80	0.06	408	18	4	0.036	1.10	1.94
		193	8-18	4.54	17.1	1.08	55	5	20	1.7	0.40	0.04	51	8	0	0.010	0.42	2.57
Norfolk fine sand (ham- mock phase)	54V	222	0-5	5.55	20.0	4.45	252	56	23	1.1	0.32	0.14	49	3	0	0.042	2.53	1.76
		223	5-18	5.81	15.1	2.73	116	27	10	0.3	0.16	0.12	42	1	0	0.020	1.66	1.65
Norfolk fine sand	54	220	0-6	4.90	17.5	5.00	256	29	85	2.0	0.32	0.24	150	4	18	0.064	3.10	1.61
		221	6-18	4.54	7.0	1.90	35	2	29	0.9	0.16	0.14	16	0.5	13	0.015	1.35	1.41

55 Grove soils	Surface soil	Minimum	4.60	17.5	1.39	149	5	21	0.2	0.08	0.06	35	4	0	0.020	0.89	1.11
		Maximum	6.59	100	6.25	1240	121	270	17.0	5.6	4.2	1840	29	77	0.073	3.10	2.39
		Average	5.56	57.3	2.72	520	39	73	3.2	0.91	0.55	408	12	13	0.039	1.56	1.73
	Subsoil	Minimum	4.29	7.0	0.68	20	1	8	0.0	0.08	0.04	6	0	0	0.007	0.42	1.17
		Maximum	5.89	48.2	3.04	212	27	68	5.3	0.96	3.0	144	22	18	0.031	1.45	2.70
		Average	5.03	17.8	1.26	66	6	26	0.8	0.36	0.26	61	6	3	0.011	0.70	1.84

\* V indicates virgin soil.

† Per acre 6 inches (2,000,000 pounds).

‡ Per 100 gm. soil.

worked out in this connection, but the phenomenon is common in the field. It is not unusual, for example, to see a tree with extremely yellow leaves and a heavy crop on all but one limb, which will have very green leaves and no fruit; conversely, one limb may be bearing a heavy crop of fruit and yellow leaves while the remainder of the tree is green, vigorous, and without fruit.

Symptoms associated with magnesium deficiency which arise, in all probability, from the debilitated condition of the tree are greatly increased sensitivity to cold and drouth, small fruit of poor quality, reduced tree size due to extensive loss of wood, intensification of other deficiencies, and a marked reduction in average production. Considerable has been published in connection with the effects of magnesium deficiency on production, but in many of the earlier experiments there were other limiting factors which affected the results. In our

TABLE 2

*Relative production of fruit by two seedy grapefruit plots, one deficient in magnesium and the other with a partial supply of magnesium*

Trees alike in 1937, and all other needed elements supplied equally to both since that time

TREATMENT	FRUIT PRODUCTION							
	1938-39	1939-40	1940-41	1941-42	1942-43	1943-44	1944-45	1945-46
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
No magnesium . . . . .	1847	37	2550	515	2055	175	..	3375
Magnesium supplied.. . . .	3576	210	4685	1000	5411	4525	..	5785

experiments, however, we have some clear-cut comparisons in which all of the needed elements except magnesium were supplied and the trees were accurately comparable in all details, including exposure to cold and drouth. Table 2 gives the production record of two such plots, which are typical of some of these experiments. The trees in these two plots were as nearly alike as possible in 1937, when they were deficient in manganese, copper, zinc, and magnesium. Starting in 1937 they have had exactly the same treatment except that one plot received no magnesium and the other received about half the normal requirement, supplied in the form of magnesium sulfate. The very large differential in production that has developed is not unusual and indicates the very beneficial effects of magnesium applications on deficient soils.

#### DISTRIBUTION OF MAGNESIUM IN PLANT

The chemistry of magnesium deficiency in citrus has been extensively investigated by Fudge (4, 5). The citrus tree has a fairly high requirement for magnesium, particularly as a constituent of the seed in the fruit. For seedy varieties of grapefruit, Fudge has found that if a tree has an adequate supply of magnesium, the dry matter of the leaves will contain about 0.3 per cent Mg, whereas the dry matter of the whole fruit will contain about 0.12 per cent and that of the seed alone, 0.19 per cent. The seeds, which represent about one tenth of the dry matter of the fruit, thus contain about one fifth of the magnesium

in the fruit. These figures are approximations, since there are considerable variations at different seasons, especially in the leaves. Fruit from Marsh Seedless grapefruit contained less magnesium, because of the reduced amount of seed. It is a curious anomaly, however, that Marsh Seedless on a magnesium-deficient soil commonly suffers less from magnesium deficiency than do the seedy varieties, but at the same time, because of its higher production, it removes more magnesium from the soil. Fudge explains this as due to the difference in the method of fruiting, but considerable recent evidence indicates that Marsh Seedless produces more vigorous root system with more ability to collect magnesium.

The mechanism by which the deficiency operates, as developed by Fudge (4), is of interest. The magnesium in the leaves is translocated to the nearby fruit during the summer and fall while the fruit is developing rapidly. Ultimately the leaves become so low in magnesium that they drop. Thus a leaf formed coincident with bloom in the spring may yellow and fall by August or September instead of remaining on the trees for the normal  $2\frac{1}{2}$  to 3 years. This condition is, to a considerable degree, localized in the neighborhood of the fruit. For instance, Fudge found, on the same tree, that green leaves on branches without fruit contained 0.15 to 0.2 per cent of magnesium in the dry matter while yellow leaves in the vicinity of the fruit contained from 0.013 to 0.017 even though they had contained as much as 0.2 per cent magnesium in the spring. The symptoms found in the fall are thus due to removal of magnesium from the leaf rather than to an initial acute shortage of magnesium which affected the growth of the young leaf, as is the case in deficiencies of manganese and zinc. Fudge (5, 6), in attempting to establish a basis for foliar diagnosis in the spring while the leaves were normal in appearance, found that if the magnesium content of the dry matter of the leaves close to the fruit was 0.35 per cent or higher in the spring and magnesium was used as recommended in the summer fertilizer, no magnesium-deficiency symptoms would develop in the fall, but, if the content was below 0.2 per cent, magnesium deficiency could be expected if only the recommended amount of magnesium was used in the summer and cropping was only light.

Reed and Haas (9) working with sand cultures showed what is apparently a translocation of magnesium from old leaves to developing leaves of a succeeding flush of growth. This is sometimes seen in the field but is not so pronounced as the effect brought on by translocation to the fruit. In only a few instances has a pronounced deficiency of magnesium in new leaves been noted in the field in Florida. In the literature on other plants, mention is made of this relationship to fruiting, though some reports point out that the older leaves develop the deficiency symptoms. We would presume from our experience that this is due to the translocation of magnesium to younger leaves.

#### CORRECTION OF MAGNESIUM DEFICIENCY

The extensive use of magnesium to correct the deficiency of this element in Florida started in the mid-thirties. Dolomite and commercial magnesium

sulfate (calcined Kieserite) were the materials primarily used at that time. It was found that applications of dolomite on acid soils (pH 4.5 to 5.0) failed to give good results in the first year but effected a marked improvement in the trees the second year, whereas the use of the soluble form gave good results almost immediately. As a consequence, a program was developed for the acid soils in which both materials were used to supplement each other. As a result of work by Peech (8), it was found desirable to raise the pH of the soil once a year to about 5.5 to 6.0. Dolomite was suitable for this purpose, since it not only raised the pH slowly and not too high but it also furnished magnesium. In these studies it was found, however, that dolomite alone was not adequate as a source of magnesium and that some soluble magnesium had to be used to supplement it. In studying the less acid soils (pH 6.0 to 8.5) it was found that dolomite gave little or no result, and soluble magnesium had to be depended upon almost entirely. As the pH of the soils in the commercial groves and experimental plots on the acid soils was raised, dolomite became progressively less valuable as a source of magnesium. Jamison<sup>2</sup> showed that dolomite reacted with the soil very slowly at a pH of 6.0 or higher and that the presence of calcium in both the dolomite and the superphosphate used in the fertilizer reacted against the development of available magnesium in the soil from dolomite and other water-insoluble magnesium compounds. It should be noted in this connection that these sandy soils are very light and have little buffer capacity; consequently, contact with particles of dolomite is poor and there is little acid to react with it. Fudge (7) had also shown that there is a marked antagonistic action between Ca and Mg and K, and that high calcium effects a reduction in the amount of magnesium and potash absorbed. Since both potash and calcium are extensively used in citrus fertilizers, it is important to supply large amounts of magnesium in an available form to balance the nutritional supply. There has been a tendency to the overuse of dolomite, with the result that the pH of the soil in many groves is higher than that recommended (pH 5.5 to 6.0). This has tended to reduce the effectiveness of both the dolomite and the other insoluble forms of magnesium such as the oxides. Jamison has shown that a material of this type, which will release 80 per cent of its magnesium in an exchangeable form in a sandy soil at a pH of 5.0, may release no more than 30 per cent of its magnesium in the soluble or exchangeable form when it is applied to a similar soil at pH 6.0, and even less in a soil of still higher pH.

The recommendations of the experiment station originally called for a certain percentage of soluble magnesium (in relation to N) in the fertilizer. When magnesium from water-insoluble sources was substituted for the soluble sulfate, however, the trees on soils with a pH of about 5.5-6.0 frequently failed to obtain sufficient magnesium and cases of mild magnesium deficiency have become common. This has served to focus attention strongly on the importance of soluble magnesium in the fertilizers for Florida citrus, whether the soluble magnesium is obtained from magnesium sulfate, from sulfate of potash-magnesia, or by

<sup>2</sup> Unpublished studies by Vernon C. Jamison, Soils chemist, Citrus Experiment Station, Lake Alfred, Florida.

the reaction of magnesium oxide or other water-insoluble forms in the base pile or in the complete fertilizer mix. Unfortunately in this connection, the custom in Florida is to mix magnesium-bearing materials with a cured nitrogen-phosphorus base plus any other needed constituents. Since fertilizers in Florida are mostly mixed to order and are frequently applied within 2 or 3 days after they are mixed there is little chance for reactions to take place within the storage pile or bag.

The question of magnesium sources must be related to the soil characteristics and to the fertilizer program followed. In tight clay soils with high total acidity the intimate contact plus the strong buffer action may greatly increase the value of a material over that of the same material on a loose dry sandy soil of low buffer capacity. It goes without saying that either an oxide or a carbonate must react with some acid material in order to produce a water-soluble form, and intimate contact with the acid constituents of the soil will produce a more rapid and complete transformation than poor contact. Where the soil is such that the conversion from water-insoluble to water-soluble is poor, then the necessity for supplying soluble magnesium in the fertilizer becomes great.

This point has been emphasized because the shortage of soluble magnesium materials is acute at present and there has been a tendency to introduce a great many alternate forms, most of them water-insoluble. Too often these forms have been evaluated on the basis of their percentage of total magnesium without due regard to the soil and fertilizer factors involved. The basic difficulty involved in the conversion of water-insoluble forms within the soil seems to revolve around the fact that as the pH approaches and passes 6.0 the rate of reaction and the percentage converted are greatly diminished, the diminution for any particular material varying with the physical and chemical state. None of such materials examined by Jamison so far have given a high rate of conversion above pH 6.0, whereas the calcium materials continued to react to a considerably higher pH. For citrus on Florida soils it seems necessary to use either a soluble magnesium material or to obtain the conversion from the insoluble to the soluble form within the fertilizer mixture. So far as Florida citrus growers are concerned, the use of magnesium in relatively large amounts is an established practice, and the important question today is: In what form is it to be applied?

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# MAGNESIUM NUTRITION OF APPLE TREES<sup>1</sup>

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Although in 1925 Wallace described the symptoms of magnesium deficiency of apple trees (16) on the basis of sand culture experiments, it was not until about 1939 that reports of magnesium deficiency in commercial apple orchards appeared in the literature. Among the earliest of such reports were those by Hill (8) in Quebec and Wallace (17) in England. Both workers based their diagnoses, not on responses to magnesium, but on the similarity of the symptoms to those produced by trees in sand cultures lacking magnesium and on the very low magnesium content of leaves from affected trees. In 1940, Kidson, Askew, and Chittenden (11) confirmed the work of Wallace and Hill, showing that leaves from apples trees exhibiting similar symptoms in the Nelson District, New Zealand, were uniformly lower in magnesium than were leaves from unaffected trees. The New Zealand workers also prevented the development of magnesium-deficiency symptoms on branches of seriously affected trees by injecting epsom salts solution, but they failed to obtain response to soil amendments of magnesium compounds. Three years later reports from Massachusetts (13) and from New York (2) indicated that magnesium deficiency was a commercial problem in some apple orchards of eastern United States. The diagnosis in New York was based not only on visible symptoms and chemical analysis but also on responses to liquid injections and to spray applications of epsom solution.<sup>2</sup> But no clear-cut responses to soil applications of magnesium materials were at first reported. In the course of these initial diagnostic studies and subsequently, some progress has been made in our understanding of the symptoms of magnesium deficiency in the apple, the soil and climatic conditions favoring its appearance, the orchard management practices aggravating the problem, and the most promising control methods.

## VISIBLE SYMPTOMS OF MAGNESIUM DEFICIENCY

The first visible evidence of magnesium deficiency in apple trees is a fading between the large veins of the older leaves on some shoots or spurs. The faded areas may turn very pale yellow and remain so for some time, or they may scorch rapidly; in either case, necrotic brown "blotches" develop from them. Some of the dead areas between veins may remain as separate islands surrounded by green tissue, but many of them tend to coalesce as they grow in size, and where they grow together at the leaf margin may produce a marginal leaf scorch indistinguishable from that resulting from potassium deficiency in its later stages. There are apparently varietal differences in the degree of yellowing

<sup>1</sup> Paper presented at the meeting of the American Chemical Society, Division of Fertilizer Chemistry, Chicago, Illinois, September 10, 1946.

<sup>2</sup> Helpful advice on concentration and timing of sprays was given by H. Hill, Central Experiment Farm, Ottawa, Canada.

prior to necrosis. The leaves of some varieties, among them Red Delicious, Golden Delicious, Cortland, and Melba, seem typically to fade to pale yellow between the veins and at the margins before showing much necrosis. Other varieties, including McIntosh, Baldwin, and Fameuse, may develop dead blotches in leaves that a few days before appeared altogether normal. It is also likely that weather, spray practices, and nutritional conditions influence the way in which the symptom patterns develop.

The older, basal leaves on shoots and spurs are usually affected first, and as the season progresses the injury appears on the younger leaves. Those first affected may shrivel and drop, and as a result by late summer shoots on which the symptoms developed early may be defoliated except for a few leaves near their terminals. Fruits on such branches tend to be small, to be poor in quality, and to drop prematurely.

The degree to which the symptoms develop on an affected tree varies greatly. Only a few branches may be affected, or the whole tree may be rather uniformly scorched and defoliated. There is likely to be great variation in the development of the injury within an affected orchard; some trees may be badly injured, whereas others may appear to be completely normal. There are also great variations in the severity of injury from year to year in the same orchard.

In general, the earlier the symptoms develop, the greater is the loss of effective leaf surface to the tree by the end of the growing season. Under New York conditions young trees very deficient in magnesium may begin to defoliate in late June and may be virtually leafless by the end of August. Such trees make weak vegetative growth and probably cannot ever become productive. It is more common, however, for the first leaf blotch to become evident after vegetative growth has stopped and flower initiation has gone on for some time (after mid-July in New York). Under these conditions, even though defoliation and leaf injury cause a serious loss of marketable fruit, there may be no stunting of vegetative growth or decrease in bloom the following year.

Trees showing magnesium deficiency appear to be very sensitive to spray injuries.

#### CHEMICAL ANALYSIS

It has already been indicated that the magnesium content of apple leaves is a helpful index of the magnesium level of the tree. The relationship between magnesium analysis and presence or absence of deficiency symptoms has been studied in England, New Zealand, and the United States (2, 4, 11, 13, 18) and the results from those areas are in substantial agreement. When the magnesium content of mature apple leaves sampled in midsummer is above 0.40 per cent MgO or 0.25 per cent Mg (dry-weight basis), trees rarely show magnesium-deficiency symptoms. When the magnesium content is between 0.40 and 0.25 per cent MgO, the leaf blotch symptoms may appear if other conditions, which will be discussed subsequently, favor their appearance. When the magnesium content falls below 0.25 per cent MgO (0.15 per cent Mg) leaf symptoms are likely to appear on some branches, regardless of other conditions. The per-

centage of magnesium in the ash of leaves is also low under deficiency conditions (9, 13, 18).

Analysis of leaves for potassium as well as magnesium may be helpful in differentiating magnesium deficiency from potassium deficiency, in indicating the soil conditions associated with the development of the trouble, and in giving indication of the most suitable control measures. If little is known of the soil conditions in orchards apparently affected with magnesium deficiency, determination of pH, exchange capacity, and exchangeable magnesium, calcium, and potassium at several depths may also be helpful.

#### CONDITIONS AFFECTING THE OCCURRENCE OF MAGNESIUM DEFICIENCY OF APPLE TREES

Though Wallace (18) has found magnesium deficiency in apple orchards of England situated on soils both high and low in calcium, the reports from elsewhere have indicated that it is usually found in orchards on acid soils low in both calcium and magnesium and often low in exchange capacity. Under acid soil conditions the potassium status of the soil and potassium fertilization may influence the magnesium nutrition of apple trees. Trees deficient in magnesium are high in potassium (as judged by their leaf content) even when replaceable potassium is rather low in the soil (2, 9, 11, 13, 18). Liberal potassium fertilization of trees on soils that are low in calcium and magnesium has been found to induce magnesium deficiency and/or to increase its severity (3, 8, 11, 13). There appear to be two reasons for this effect of potassium. It inhibits the absorption of magnesium by apple tree roots, and over a period of years it decreases the amounts of replaceable calcium and magnesium in the soil exchange mechanism (3).

Broadcasting ammonium sulfate under apple trees and spraying or dusting them with sulfur have resulted in marked acidification of the soil under the spread of the branches (1, 3, 15). It is not uncommon in New York apple orchards for the pH of the surface soil under the trees to be close to 4, and to be more than a unit below that between the trees. This increase in acidity has resulted primarily from loss of replaceable calcium and magnesium (3); depletion of these nutrients in soils initially acid and low in exchange capacity may well be aggravating the problem of magnesium deficiency in some orchards.

Nitrogen fertilization seems to some degree to decrease the prevalence and severity of magnesium deficiency in apple orchards. Observations by Wallace (18) and by Hoblyn (10) in England and by Boynton and Compton (5) in the United States have indicated that magnesium-deficient trees under high nitrogen fertilization show less leaf blotch than paired trees given less nitrogen fertilizer or none. Chemical analyses by Boynton and Compton (5) show a positive correlation between leaf nitrogen and leaf magnesium in trees differentially fertilized with nitrogen.

There is some evidence that heavy rainfall during the growing season may favor the development of magnesium-deficiency injury to apple leaves. Thus, Hill and Johnston (9) reported that the symptoms were particularly prevalent

in Quebec in 1938 following prolonged summer rains; Wallace (18) found the greatest development of symptoms in 1939, a year of large crop in which July rains were heavy in England; Boynton, Cain, and Compton (4) found magnesium-deficiency blotch to be more prevalent and severe in New York apple orchards in 1942, a year of high rainfall, than in 1941 when rainfall was below normal. The New York workers sampled leaves from specific trees in 148 McIntosh apple orchards in July of both years and found the magnesium content was significantly lower in the year of high rainfall. Other climatic influence may be involved but as yet have not been studied carefully.

#### CONTROL MEASURES

A number of magnesium carriers have been applied to the soil in efforts to control magnesium deficiency of apple trees. More often than not, little or no benefit has been observed in the first year following treatment (2, 8, 11, 13, 17). If enough material was applied, partial recovery has usually been observed in the second year after soil application (2, 6, 12, 14). But recovery has not always been complete even after 3 years of rather heavy magnesium fertilization. The slow and sometimes incomplete recovery apparently results from failure of the roots to absorb enough magnesium to restore normal tree behavior. In some instances thorough mixing of the material with the soil and application on mulching materials have seemed to improve intake and recovery (6, 14).

The evidence on efficacy of the different carriers used under acid soil conditions is conflicting. Epsom salts, kieserite, salt water magnesia, magnesium carbonate, and dolomitic limestone have all caused improvement of trees suffering from magnesium deficiency (6, 12, 14); the limited tests made thus far do not permit ranking these materials according to effectiveness. Dolomitic limestone has, in some instances but not always, appeared to be slower in action than the other materials (6, 12, 14). "Fortification" of the dolomitic limestone with epsom salts has sometimes but not always seemed to cause greater increase in leaf magnesium than dolomitic limestone alone (6, 14). The use of low-magnesium limestone has not benefited trees suffering from magnesium deficiency and in some instances has appeared detrimental (12).

It seems likely that a fertilizer program designed to eliminate magnesium deficiency in apple orchards will have to take into account the calcium status of the soil as well as its magnesium content. Where the soil is acid and low in calcium the use of dolomitic limestone along with other magnesium carriers would seem to be advisable. Provision should be made, furthermore, to get a good deal of the limestone spread evenly under the trees where acidification has been most rapid. On the other hand, where calcium is already high in the soil and acidity is low, as Wallace has suggested (18), dolomitic limestone, magnesium carbonate, and magnesium oxide probably should not be used. In either situation, particularly where exchange capacity is low, potassium fertilizers should not be used unless there is direct evidence of potassium deficiency in the orchard, and in either situation a relatively high level of nitrogen should be maintained in the trees.

Experiments in New York (2, 6), Massachusetts (14), and Maine (7) have indicated that sprays including epsom salts can be used as effective control measures for magnesium deficiency of apple trees. When 20 pounds of epsom salts per 100 gallons of water was used by the Massachusetts and Maine workers in three regular cover sprays including arsenicals and fungicides, commercial control of the trouble was apparently attained without loss of effectiveness of the spray in controlling insects and diseases and without development of spray injury. In New York such a mixture of epsom salts with the summer arsenical and flotation sulfur spray in a Baldwin apple orchard caused severe defoliation in one year, apparently due to arsenical injury (6). Separate sprays of epsom salts solution, however, controlled blotch without causing leaf injury. Because of the slowness of response to soil applications, there seems to be a place for spray treatments of epsom salts in apple orchards severely affected by magnesium deficiency. Whether spray applications will be used only in the period before soil treatments have taken effect, or will be used as permanent control practices, remains to be seen.

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## EFFECT OF MAGNESIUM ON GROWTH AND COMPOSITION OF TOBACCO<sup>1</sup>

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Magnesium has long been recognized by the plant physiologist as belonging to the group of chemical elements indispensable for normal growth of plants. It is only within the last 25 years, however, that this element has been recognized as of any significance in practical fertilizer usage. The first paper pointing out its importance was published in 1922 (8), and a more detailed account followed in 1923 (9).

The continuing trend in the fertilizer industry, largely on the basis of economic considerations, is toward the use of refined chemicals to supply in highly purified form and relatively free from "filler" or material generally thought to be inert, the three elements nitrogen, phosphorus, and potassium, which erroneously have been generally considered as furnishing a complete fertilizer. Mixtures of potassium nitrate and an ammonium phosphate or of ammonium nitrate and a potassium phosphate are examples of such high-analysis mixtures. It has been clearly demonstrated by experimental evidence and by observation that such mixtures do not produce normal growth on some of the important tobacco soils. The best evidence available indicates that the elements supplied in these compounds function normally but that additional elements are required for normal growth. Apparently lack of magnesium, as well as calcium and in some instances sulfur and the microelements boron, copper, zinc, and manganese, in such mixtures operates to limit growth.

### MAGNESIUM AS A PLANT NUTRIENT

In problems of fertilizer usage the significance of the magnesium supply of the soil has received such inadequate attention in this country that it will be of interest to review briefly the early literature on magnesium as an essential plant nutrient.

As early as 1849 and 1851 Salm-Horstmar (30, 31) conducted pot experiments with the oat plant in which sand and charcoal derived from pure sugar were used as culture media. It was found in these experiments that magnesia is one of the necessary ash constituents of the plant. In its absence only the first three leaves of the plant had a normal green color while the others were of a greenish-yellow

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color, and the plants died without fruiting. The stems were weak, and had a tendency to fall over. Pasteur (26) in 1868 recognized magnesium as one of the essential nutrients for the acetic acid ferment (*Mycoderma aceti*). A year later Mayer (19) reached the conclusion that in all probability the yeast plant must be supplied with magnesium for its normal nutrition. Molisch (21) demonstrated that this element is indispensable for all the higher fungi with which he worked and showed that it cannot be replaced by calcium, barium, or other metal. Investigators are agreed that magnesium must be included in the nutrient medium for algae. In its absence Bokorny (3) noted a contraction of the cell nucleus. According to Servittaz (33) magnesium is one of the indispensable metals for the nutrition of mosses.

As early as 1869 Dempwolf (7) showed that magnesium tends to follow protein distribution in plant tissues and accumulates particularly in the seeds, in contrast with calcium, which tends to accumulate in foliage leaves. Willstatter (37) found that the magnesium content of cereal seeds always exceeds the content of calcium. The magnesium content of the seed proper commonly exceeds that of the seed covering, whereas the reverse relation holds true for calcium and, moreover, the magnesium content of the former does not vary very widely. The nutritive tissues of the seed frequently contain more magnesium than do the green assimilating parts of the plant. During the ripening of seeds there is a progressive increase in content of magnesium and phosphorus while there is a decrease in total ash. Underground storage organs usually contain less than 10 per cent of total ash, and magnesium as a rule makes up less than a tenth of the ash. According to Shibata (34), in the early growth of bamboo, magnesium and phosphorus are quickly translocated from the rhizome to the growing point and are easily recognized in the procambial strands. The ash of the wood of trees usually carries somewhat more than 3 to 6 per cent magnesium. In older bark of trees the magnesium content of the ash is very low, usually not more than 1 to 3 per cent, but the content in young bark is considerably higher. In foliage leaves, the magnesium content of the ash is subject to wide variation but at times exceeds that of the nutritive tissues of the seed. A number of investigators have shown that frequently the magnesium content increases as the leaves grow older, although this does not always hold true. In fibrous roots the ash content commonly increases with age, primarily because of accumulation of calcium, but the content of magnesium tends to decrease.

Benecke (2), as well as Molisch, has demonstrated that magnesium cannot be replaced by calcium, barium, or other metal in the culture medium for fungi. Magnesium appears to be an essential constituent of the cell plasma and of the reserve proteins. As is true of most other essential elements, its specific functions are only partly understood. Salm-Horstmar (31) observed a loss of the normal green color in his cultures when magnesium was withheld, and Raumer (28) observed a marked blanching of the leaves as a result of withholding magnesium in cultures of *Phaseolus multiflorus*. This latter investigator believed that magnesium functions in the transport of starch and other nutrients, in addition to its function as a constituent of chlorophyll. Reed (29) observed that in *Sprygyra*

the nucleus divides mitotically in the absence of magnesium in the nutrient medium, but in *Vaucheria*, formation of oil in the chlorophyll bodies could not be detected. The ratio between magnesium and phosphorus seems to affect the functioning of the latter. Loew (14) likewise considered that magnesium functions as a carrier of phosphorus. The epoch-making researches of Willstätter (36, 37, 38) on chlorophyll first brought clearly to light one of the specific functions of magnesium. It was definitely shown that this element is an essential constituent of the green chlorophyll pigment. That it has other important functions is shown by the fact that it is indispensable in the nutrition of lower organisms.

#### TOXICITY OF MAGNESIUM

The toxic action of magnesium on plants under certain conditions attracted attention long before the element had been recognized as an essential nutrient. Writing in 1799, Tennant (35) pointed out that a certain lime when applied in large quantity had been found to lower the productivity of the soil, whereas even larger quantities of lime from other sources were beneficial. The lime in question was composed of 3 parts calcium oxide and 2 parts magnesium oxide. In the form of powdered limestone this product did not affect germination or the growth of seedlings but after having been calcined and then exposed to air for several weeks it caused marked injury. Other limestones similarly treated failed to produce injury. Similarly, as compared with lime from marble, calcined magnesia was decidedly toxic to seedlings in sand cultures, although the toxicity was reduced by the presence of vegetable matter. Some injury also was obtained with uncalcined magnesia. Sir Humphry Davy (6) observed that magnesium carbonate when spread on grassland caused no injury. He considered that the injurious action of calcined magnesia was due to the slowness with which it combines with carbon dioxide, thus losing its caustic properties. De Candolle (5) also pointed out that many soils containing considerable quantities of magnesium are highly productive and soils composed largely of disintegrated dolomite do not seem to be less productive than other soils. Petzholdt (27) referred to certain areas of salt soil (Salzboden) in Poltawa and Tchernigov which in appearance seemed to be identical with surrounding highly productive soils but produced poor crops, especially of grasses and small grains. The low productivity was ascribed to an excess of magnesium over calcium in the soil. In this connection, however, Gordon and Lipman (12) have suggested that lack of fertility of serpentine soils is due to deficiency of certain ions and a high pH rather than to a high content of soluble magnesium. Working with cultures of *Phaseolus multiflorus* in solutions of single salts, Wolf (39) obtained an excellent growth of roots with calcium sulfate, but with magnesium sulfate the roots quickly became unhealthy and lost their turgidity and the root cells became inactive. Raumer (28) in cultures with the same plant found that in distilled water and in solutions containing neither magnesium nor calcium, plants grew better than when magnesium was present and calcium absent. Boshm (4) and Atterberg (1) confirmed Raumer's data indicating that magnesium salts are toxic when an adequate

supply of calcium is not present. Schimper (32) showed that neutral potassium oxalate is highly toxic to green plants. Moreover, lack of calcium produces all the symptoms of poisoning and by a product formed chiefly in the growing tip and foliage leaves. Under these conditions the affected tissues are very rich in soluble oxalates. Hence, it is concluded that the primary function of calcium is to precipitate the toxic oxalates. Loew (14) confirmed Schimper's results and further demonstrated the toxicity of magnesium in the absence of calcium. He considered that calcium is an essential component of protein compounds in the cell nucleus and in the chloroplast and that there is a certain analogy in the toxic action of soluble oxalates and magnesium. The former abstracts calcium from these protein compounds, while the latter tends to replace the calcium in them when the calcium supply is relatively low.

The investigations referred to in the preceding paragraphs demonstrate three facts: (a) Magnesium is an essential nutrient for all plants; (b) under certain conditions this element is highly toxic to green plants; (c) calcium in suitable concentration may effectively overcome the toxicity of magnesium. On the basis of these facts and the additional consideration that calcium, likewise, is an indispensable nutrient for all the higher plants, Loew formulated his theory of the "lime factor" for plants. This theory postulates that for best results plants require a fairly definite ratio between calcium and magnesium in the soil, this optimal ratio varying considerably for different plant species. Loew's theory attracted wide attention among investigators, and an extensive literature has developed on the subject. For present purposes, however, it is not necessary to consider further the status of this problem except to say that, though investigators are not in agreement in their interpretations, their results on the whole seem to indicate that under varying and complex field conditions the optimal lime-magnesia ratio is not so narrowly defined as originally formulated by Loew and co-workers. That the theory is sound in principle, however, practically follows from the premises. In at least some respects, this doctrine is but a special case of the general principle of physiological antagonism later developed by Loeb (13) for the animal organism and by Osterhout (25) for the plant. It appears, however, that among the primary nutrients magnesium is outstanding in its toxic tendencies and calcium likewise is outstanding in its capacity for counteracting this toxicity.

#### SYMPTOMS OF MAGNESIUM DEFICIENCY IN TOBACCO AND OTHER PLANTS

The outstanding symptom of an inadequate supply of magnesium in higher plants is a loss of the normal green color (8, 18), which is usually most evident in the foliage leaves. This breaking down of the chlorophyll pigment in plants when magnesium is withheld from the culture medium was observed by early investigators, but the characteristic features of the blanching effect and its results as seen under field conditions apparently had received little attention prior to publication of the paper from this office on the so-called sand drown disease of tobacco (9, 16), which was shown to be due to magnesium hunger. Because of the enormous leaf development of tobacco and the rapidity of its

growth, this plant is admirably adapted to study of the phenomena associated with magnesium deficiency. The fact that breaking down of the chlorophyll is the first clearly discernible symptom of magnesium hunger seems to indicate that there is a certain minimum requirement for magnesium in the plant as a whole which must be supplied before the additional need for the functioning of chlorophyll can be met. In other words, when the magnesium supply becomes inadequate, the chlorophyll pigment seems to be the first constituent of the green plant to suffer. Moreover, it is an interesting fact that the yellow as well as the green pigments are involved, and the blanched areas of affected leaves tend to assume a very light yellow or almost pure white color.

The loss of color begins in the lowermost leaves of the plant and at the tips of affected leaves. This loss of color advances along the margins and inwardly between the veins of the leaf, and as the disease increases in severity it advances progressively from the lower leaves of the plant upward. The larger veins of the leaf tend to retain their green color except in severe cases. As a rule, the growth relations of the different organs and tissues of the plant are not greatly disturbed, and affected leaves tend to remain smooth and show little tendency toward specking or development of dead spots. Even in cases of severe magnesium hunger the plant is able to flower and develop seed.

Blanching or yellowing of the leaf may result from a variety of causes, but most of these effects are readily distinguished from the phenomena of magnesium hunger. This malady, however, is likely to be confused with potassium hunger unless due attention is given to certain distinguishing features. As already mentioned, the specking or localized breaking down of tissue so commonly seen in potassium hunger rarely occurs in cases of magnesium deficiency. In the former condition the tip and margins of the leaf curve downward in characteristic manner, the margins often become broken and ragged, and the leaf commonly assumes a rough, savoyed form of development. None of these effects are seen in magnesium hunger. In contrast with the pale yellow or almost white appearance of affected areas and the normal green of the remainder of the leaf seen in magnesium hunger, in potassium hunger the bleached areas of the leaf show a deeper, dull yellow with a bronze overcast, and the remainder of the leaf usually has an abnormally dark bluish green color. In the cured tobacco leaf, evidences of magnesium deficiency are most marked in the flue-cured type which normally has a bright yellow color. After the curing the diseased portions of the leaf are abnormally thin and nonelastic, have a dry papery texture, and usually show a dull, lusterless light brown color. In some types of tobacco the contrast in color with that of the normal leaf is less clearly defined. These symptoms have been observed on tobacco plants at all stages of growth from the young seedling in the seedbed to the mature plant in the field.

In other plants the symptoms of magnesium hunger are more or less similar to those seen in tobacco (10, 17), but in general the trouble is not so readily diagnosed. In corn the lower blades of the plant show a striped effect due to breaking down of the chlorophyll in the areas between the veins. The distinc-

tions between magnesium hunger and potassium hunger are, in general, similar to these in tobacco. In soybeans the leaf presents an appearance clearly suggestive of that seen in tobacco. A tendency of the lower leaves to shed, however, interferes with full development of deficiency symptoms. There seems to be an interesting distinction in the case of cotton. Instead of the bleaching effect due to decomposition of chlorophyll, development of anthocyan results in the upper surface of the leaf's assuming a bright red appearance. The under surface of the leaf, however, tends to retain its green color.

#### EFFECTS OF MAGNESIUM ON COMPOSITION OF TOBACCO

The actual content of magnesium in tobacco leaves manifesting magnesium deficiency (10, 11) may vary from 0.08 to 0.20 per cent, the most severe symptoms becoming evident with the lowest percentage (0.08–0.10 per cent), and well-defined symptoms, at a higher percentage (0.15 per cent). Leaves containing 0.22 and 0.27 per cent showed no visible symptoms of magnesium deficiency. It appears, therefore, that a leaf containing around 0.25 per cent may be expected not to show visible symptoms of the deficiency. It has been estimated (38) that the leaf should contain 0.03 per cent magnesium to satisfy the amount contained in the chlorophyll. It appears, therefore, that there are other functions of magnesium which must be met before those required only for chlorophyll.

The amount of magnesium in tobacco leaves seldom exceeds 0.6 per cent on light soils, but it may be as high as two or three times this amount on heavy soils or where readily available magnesium is applied to light soils. The percentage contained in the stalk or other plant parts may be as low as 0.1 or as high as 1. When the plant is suffering from magnesium deficiency the lower leaves commonly contain less magnesium than the upper leaves; but when magnesium is supplied liberally, the lower leaves may contain more magnesium than the upper leaves.

The higher ash content of magnesium-deficient leaves in comparison with normal leaves probably is a result of the low carbohydrate, but there is also an increase in the calcium content.

Leaves manifesting severe symptoms of magnesium deficiency have a higher water content and on drying will show less dry matter than normal leaves and a lower weight of dry matter for a given green leaf area. The starch content is lower, apparently because of failure of the photosynthetic processes associated with the destruction of the chlorophyll. There is apparently an increase in the organic acids, probably in the form of the calcium salts.

The yield and quality of the tobacco crop will be lowered in proportion to the acuteness of the shortage of magnesium. It has been found in actual trials (23, 24) at Oxford, North Carolina, over a period of years that where magnesium was limiting, the yield was reduced as much as approximately one fourth and the gross value per acre by about one third. The average value per pound was 3 to 4 cents higher where magnesium was supplied than where the element was omitted. The evident changes due to magnesium shortage, which are most apparent in flue-cured tobacco, involve irregular colors, loss in weight, and

lack of body and elasticity. The reduced starch content would possibly result in low sugar content as well.

#### MAGNESIUM REQUIREMENTS FOR TOBACCO

Magnesium deficiency is generally most prevalent on deep sandy soils and during seasons of excessive rainfall. It was because of this relation that the name "sand drown" was associated with the deficiency.

When the soil does not supply enough available magnesium to the growing tobacco, the plant exhibits the characteristic growth effects previously described. Durham coarse sandy loam (10) at Oxford, North Carolina, was found to have the lowest (0.024 per cent) magnesium content of any soils studied. Though Merrimac sandy loam surface soil also produced tobacco showing magnesium deficiency, it contained ten times the percentage of magnesium, or 0.24 per cent.

The application of 12 pounds of magnesium per acre as sulfate or chloride corrected all evidences of the deficiency. Applications of ten times this amount of the elements in the form of magnesium limestone did not always correct the deficiency. This appears to be influenced by the fineness to which the limestone is ground. Magnesium limestone has not proved to be an ideal source of the element under all conditions, since in some cases the rates at which it is necessary to apply this material may change the soil reaction (22) to such a degree that black root rot becomes a problem.

Organic materials, such as cottonseed meal or barnyard manure, of plant or animal origin, when supplied in sufficient amounts, have proved effective sources of magnesium to prevent deficiency symptoms in tobacco when grown on soils low in available magnesium.

It has been found (15, 24) that calcite depresses the solubility of magnesium in the soil.

#### SUMMARY

The importance of magnesium as a field fertilizer was first recognized for tobacco. The characteristic symptoms of magnesium deficiency were called "sand drown" before the cause of the condition was known. The deficiency is characterized by a loss of green color in the lower leaves of the plant, beginning at the leaf tip and progressing inward along the margins and between the veins. It may be evident on plants at any stage of growth from the small seedling to maturity.

When leaf tobacco contained about 0.15 per cent magnesium, deficiency symptoms were usually evident, whereas leaves containing 0.25 per cent of the element were generally free of symptoms. High ash content is associated with magnesium deficiency. The green leaf is high in moisture and organic acids. The starch reserves of the green leaf are low when magnesium deficiency is severe. Yields have been reduced by about one fourth and gross values by about one third when magnesium shortage was acute.

Magnesium deficiency is commonly most evident on light sandy soils and following periods of excessive rainfall. Soils of different series varying in

magnesium content from 0.024 per cent to ten times this figure have been found to manifest the deficiency. An application of 12 pounds of available magnesium has been found sufficient to correct magnesium deficiency on the aforementioned soils; when magnesium limestone was the source it was necessary to supply considerably larger quantities.

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## THE MAGNESIUM-SUPPLYING POWERS 20 NEW JERSEY SOILS<sup>1</sup>

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Magnesium occurs in the soil in water-soluble, exchange, fixed, and primary-mineral forms. Wiegner and Jenny (10) pointed out that it is the most difficult of the divalent cations to displace from the soil complex, the order of difficulty of displaceability being  $Mg < Ca < Ba$ , which is identical with that of the insolubility of the hydroxides of these elements. According to these authors a colloidal particle adsorbs anions and cations in a surrounding electrical double layer the inner portion of which consists partly of OH ions that tightly bind any Mg ions that may be present.

In electrodialysis studies Mattson (7) and Prince and Toth (8) found that the percentage of exchange Mg released was relatively low in comparison with the other exchange cations. This indicates a high degree of stability of the Mg-silicate complex. When exchange Mg was extracted by the use of such salts as  $NH_4Cl$ , the above order of displaceability of the cations was confirmed.

Prince and Toth (9) examined a soil that had been repeatedly treated with dolomitic limestone for 28 years and reported that between 3 and 4 per cent of its total Mg was released by salt-extraction methods, in comparison with about 30 per cent of its total calcium. In working with synthetic complexes, Kardos and Joffe (5) and Mattson (7) found that Mg was fixed in a relatively insoluble form.

Further information on the tenacity and extent of fixation of Mg when added to the soil in the carbonate form was supplied by MacIntire, Shaw, and Robinson (6). These authors postulated two types of acid complexes in the soil. One of these quickly adsorbed Mg and held it in readily releasable exchange condition. The other reacted over a more extended period to form a complex from which the Mg was not released by conventional methods, although it could be extracted by successive shakings with 0.02 N nitric acid. In general, the work on Mg indicates that considerable amounts of this cation are withdrawn from the soil solution and fixed by the soil. The mechanics of Mg fixation is, however, still a subject of controversy.

The southern part of New Jersey is on the Atlantic Coastal Plain where the soils are naturally lacking in Mg minerals. Furthermore, by reason of their sandy texture, they are subject to serious losses of the element through the leaching action of the heavy rainfall of that area. In contrast, the soils of the

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northern part of the state are derived from glaciated shales, limestones, sandstones, granites, and gneisses and contain considerable amounts of such Mg minerals as magnesite, dolomite, olivine, and serpentine. Being heavier in texture than those of the Coastal Plain, these soils are able to retain more Mg in their exchange complexes.

In the light of these conditions it seemed desirable to determine the Mg-supplying powers of some of the more prominent New Jersey soils. A-horizon samples of 20 soil types that are being carefully investigated on a profile basis were used in this study. The general procedure was to subject the soils to the continuous action of alfalfa plants and then to determine the content of the element under investigation in both the tops and roots of these plants. In addition the soils were examined for exchangeable Ca, Mg, and K, both at the beginning and the end of the test. Although conditions are materially altered by moving field soils to the greenhouse, the values obtained by this method have been found very useful for comparative purposes.

#### OUTLINE OF EXPERIMENT

Large samples of the virgin soils were obtained from typical areas and prepared by passage through a 4-mesh screen for greenhouse use. Two-gallon, solid-bottom pots were employed as containers, 17 pounds of moist field soil being placed in each pot. Each soil was adjusted to its calculated optimum moisture content, which was set at 50 per cent of its moisture-holding capacity as determined by the Hilgard method. The actual dry weight of soil (105° C.) for each set of pots is recorded in table 4.

All fertilizer applications were made on the basis of 17 pounds soil, using C.P. salts. The lime-requirement to pH 7.0 was calculated for each soil, and  $\text{CaCO}_3$  was added as needed to adjust it to that value. Phosphorus was supplied as  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  at a rate of 200 pounds  $\text{P}_2\text{O}_5$  per 2 million pounds<sup>3</sup> soil, and an equivalent amount of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was added. Each pot was also supplied with a constant amount of KCl equivalent to 200 pounds  $\text{K}_2\text{O}$  per acre. In addition each pot received a solution containing salts of boron, copper, zinc, iron, and manganese. These elements were supplied at rates chemically equivalent to 20 pounds borax per acre for all soils except two of the triplicate pots of Sassafra and Lakewood sands, which received only 5 pounds borax and correspondingly lower amounts of the other minor elements.

The experimental variable was Mg, which was added to the natural soil at rates of 0, 94, and 188 mgm. Mg per pot to the 0-Mg, 1-Mg,<sup>4</sup> and 2-Mg series, respectively. The Mg was supplied in solution as  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , the treatments being equivalent to 0, 40, and 80 pounds MgO per acre. All fertilizers were thoroughly mixed with each lot of soil before it was placed in its pot and before any supplemental water was applied.

<sup>3</sup> Hereinafter called an "acre," since the plow depth of an average acre of soil weighs about that amount.

<sup>4</sup> Although crop-yield data were obtained from the 1-Mg series, no special studies of crops or soils of that series were made, the relative yield values being essentially the same as those of the 2-Mg series.

Alfalfa was chosen as the experimental crop because it is a vigorously growing perennial that thrives under greenhouse conditions and collects its own nitrogen. Thirty inoculated seeds of the Atlantic variety were planted in each pot on March 31, 1943. The seedlings were gradually thinned until four uniform plants remained on May 12.

At regular intervals throughout the experiment the original optimum-moisture weight of each pot of soil was restored by the addition of distilled water. These intervals were weekly in the summer and biweekly in the winter. A uniform quantity of water, determined by weighing a half dozen pots and calculating their average loss in weight, was added to each pot between these intervals whenever the condition of the soils or plants seemed to indicate the need for it. At each regular watering the pots were rotated on the benches in such a manner as to equalize as nearly as possible the light and other environmental factors.

Successive crops were harvested on June 9, July 8, August 5, September 16, November 26, 1943, and on January 28, March 17, and April 28, 1944. At the end of the experiment the alfalfa roots were screened from the soil and then washed, dried, and weighed.

Each treatment was triplicated. Since there were 20 soils and three rates of Mg application for each soil, 180 pots were involved. The produce of each pot was oven-dried and weighed separately, but the triplicates were combined before being milled for analysis. Similarly the soil of the triplicate pots was combined and mixed before being sampled for final laboratory examination. The chemical analyses in this report, therefore, are for combined triplicate samples, whether of soils or crops.

The soils were analyzed for total Mg, exchange capacity, exchange-cation content and pH values, both at the beginning of the experiment and at its conclusion. Determinations were made of the amounts of Mg, Ca, and K in the first and eighth crops and also in composited<sup>5</sup> samples of the eight crops.

#### RESULTS AND THEIR INTERPRETATION

Analytical data for the 20 soils as they came from the field are shown in table 1. Also included in this table are the pH values of the soils and their content of exchange Mg at the beginning and of the experiment.

The pH values of the original field soils varied between 3.9 for Sassafras sand and 7.7 for Hagerstown loam. Although all soils having pH values lower than 7.0 were limed at the start of the test, the pH values of approximately half of them had fallen below 6.5, and those of Lakewood and Sassafras sands had dropped to 4.6 and 4.7, respectively, by the end of the experiment. The exchange capacity of the soils varied between 2 m.e. per 100 gm. for Sassafras sand and 20 for Penn silt loam.

The total Mg in these soils varied between 2 m.e. per 100 gm. in Lakewood sand and 96 m.e. in Fox gravelly loam. If the limiting factor in the series receiving no Mg is assumed to be a lack of this element, as it was designed to be, the highest yielding soil on the basis of its content of total Mg should have

<sup>5</sup> In compositing the samples, the quantities added from each harvest were proportioned to the average yield for that harvest, treatment by treatment and soil by soil.

been the Fox. Table 2, in which the soils are arranged in accordance with their crop-producing powers without the supplemental use of Mg, reveals, however, that the Fox soil ranks twelfth in the list. No correlation was found to exist between the total Mg content of these soils and their yielding capacity. The five soils of limestone or calcareous shale origin, namely, Dover, Dutchess, Fox, Hagerstown, and Hoosic, were among the highest in total Mg.

TABLE 1

*Total Mg,\* exchange capacities, and percentage Mg saturation of exchange complexes of soils at start, and soil pH values and exchange cations at beginning and end of test*

SOIL†	pH VALUES		TOTAL Mg ORIGINAL SOILS	EXCHANGE CAPACITY ORIGINAL SOILS	EXCHANGE CATIONS IN SOILS‡ AT START OF TEST			PORTION EXCHANGE CAPACITY SATISFIED BY Mg	EXCHANGE CATIONS IN SOILS AT END OF TEST						
	Original field soils	Soils at end of test§							0-Mg			2-Mg			
					Ca	Mg	K		Ca	Mg	K	Ca	Mg	K	
	m.e.		m.e.	m.e.	m.e.	m.e.	per cent	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.		
Collington loam.....	4.7	5.8	29	16	11.47	1.12	0.69	7.0	9.95	0.72	0.19	9.78	0.94	0.15	
Dover loam.....	7.3	6.9	40	14	8.39	3.51	0.43	25.0	8.11	2.75	0.11	8.27	3.00	0.10	
Hoosic loam.....	6.9	6.9	57	11	16.43	0.96	0.35	8.7	9.04	0.76	0.13	9.37	0.90	0.11	
Lansdale silt loam.....	4.6	6.2	30	13	11.68	0.85	0.57	6.5	8.25	0.40	0.11	8.45	0.58	0.21	
Washington loam.....	4.6	5.4	36	11	8.47	0.73	0.38	6.6	6.59	0.48	0.11	6.74	0.53	0.07	
Dutchess shale loam.....	7.2	6.5	73	15	11.57	1.35	0.91	9.0	11.75	0.96	0.21	12.19	1.20	0.19	
Penn silt loam.....	4.5	5.6	83	20	12.36	1.08	0.62	5.4	10.41	0.49	0.19	10.50	0.32	0.18	
Whippansilty clay loam...	5.2	6.8	29	9	8.28	3.01	0.35	33.4	8.70	2.44	0.10	8.81	2.47	0.09	
Gloucester loam.....	5.4	6.1	43	12	8.31	0.90	0.33	7.5	6.97	0.41	0.08	6.98	0.60	0.05	
Bermudian silt loam.....	6.1	5.6	61	13	8.82	2.13	0.39	16.4	7.72	1.61	0.01	7.93	1.73	0.08	
Papakating stony loam....	5.6	6.4	66	9	6.73	0.60	0.54	6.7	6.29	0.35	0.11	6.20	0.39	0.10	
Fox gravelly loam.....	7.4	7.5	96	9	7.04	3.28	0.39	36.4	6.79	3.02	0.01	6.89	3.42	0.10	
Merrimac silt loam.....	4.4	7.1	31	10	8.67	0.82	0.34	3.2	6.74	0.15	0.01	7.01	0.43	0.06	
Chester loam.....	5.8	6.8	24	11	6.95	2.44	0.38	22.2	6.50	1.80	0.16	6.53	1.96	0.20	
Hagerstown loam.....	7.7	7.6	72	17	13.46	4.69	0.43	27.5	13.08	3.86	0.16	12.73	4.14	0.13	
Sassafras loam.....	4.5	5.3	26	8	6.29	0.22	0.44	2.8	4.86	0.16	0.09	4.78	0.32	0.08	
Colts Neck sandy loam....	4.2	5.4	30	10	5.76	0.25	0.34	2.5	4.70	0.18	0.17	5.07	0.23	0.08	
Sassafras loamy sand.....	4.4	5.7	11	3	2.74	0.13	0.27	4.0	2.02	0.13	0.05	2.03	0.13	0.04	
Lakewood sand.....	4.4	4.6	2	3	1.72	0.11	0.22	3.7	1.05	0.11	0.01	1.08	0.18	0.01	
Sassafras sand.....	3.9	4.7	7	2	1.55	0.10	0.21	5.0	0.89	0.08	0.01	1.11	0.21	0.04	

\* Total Mg and all exchange values are expressed as milliequivalents per 100 gm. soil. One m.e. Mg is equivalent to 0.01216 per cent Mg, or 243.2 pounds per 2 million pounds soil.

† With the exception of Dutchess, Fox, Hagerstown, and Hoosic, these soils came from areas that were believed never to have been farmed.

‡ At the start of the experiment, soils were brought up to about pH 7.0 with  $\text{CaCO}_3$ , except where original pH values were above this point.

§ These values were obtained on soil from the 2-Mg series of pots.

|| The Ca and K values include not only the original amounts present in the soils but also those that were added. An application of 0.21 m.e. available K per 100 gm. soil, equivalent to 200 pounds of  $\text{K}_2\text{O}$  per acre, was made to each soil. On the 2-Mg series, 0.2 m.e. available Mg per 100 gm. soil, equivalent to 80 pounds  $\text{MgO}$ , was added.

The data in the column in table 1, labeled "Portion Exchange Capacity Satisfied by Mg," furnish a partial index to the Mg-supplying powers of these soils. All but one soil that had less than 6 per cent of the exchange capacity thus satisfied, namely, the Penn, Merrimac, Sassafras loam, Colts Neck, Sassafras loamy sand, and Lakewood, responded to additions of Mg. Sassafras sand was the only exception (table 2, column 4). This may be explained by a number of possible limiting factors, including insufficient amounts of trace

elements, low pH values for the later crops, and low amounts of exchange Ca. Soils having the highest percentage saturation of Mg in the exchange complex, namely, the Dover, Whippany, Bermudian, Fox, and Chester, tended to be the least responsive to Mg additions. An exception to this tendency was found in the Hagerstown soil, which showed marked response to Mg additions.

TABLE 2

*Total dry yield and Mg content of composited samples of tops and roots of eight crops of alfalfa grown on 20 New Jersey soils with and without added Mg*

SOIL*	WEIGHT OF TOPS			Mg in TOPS		WEIGHT OF ROOTS		Mg in ROOTS	
	0-Mg	2-Mg†	Increase from 2-Mg	0-Mg	2-Mg	0-Mg	2-Mg	0-Mg	2-Mg
	gm.	gm.	per cent	per cent	per cent	gm.	gm.	per cent	per cent
Collington.....	69.2	68.0	-1.7	0.31	0.32	31.0	31.7	0.22	0.24
Dover.....	63.6	58.0	-8.8	0.50	0.40	25.7	21.3	0.37	0.39
Hoosic.....	59.3	52.3	-11.8	0.37	0.33	23.3	28.7	0.42	0.44
Lansdale.....	59.1	56.6	-4.2	0.36	0.26	21.3	28.7	0.27	0.26
Washington.....	58.6	60.8	3.8	0.31	0.30	35.7	46.3	0.25	0.29
Dutchess.....	57.8	56.8	-1.7	0.36	0.33	36.0	36.3	0.42	0.43
Penn.....	57.1	63.2	10.7	0.29	0.23	29.7	35.0	0.29	0.38
Whippany.....	53.5	48.6	-9.2	0.52	0.53	20.7	19.3	0.38	0.38
Gloucester.....	47.3	55.6	17.6	0.35	0.36	22.0	23.7	0.29	0.30
Bermudian.....	45.8	44.4	-3.1	0.43	0.47	26.0	23.3	0.40	0.39
Papakating.....	43.7	42.0	-3.9	0.34	0.34	18.0	25.7	0.42	0.52
Fox.....	43.0	44.4	3.2	0.59	0.64	17.7	19.7	0.65	0.58
Merrimac.....	41.5	48.9	17.8	0.21	0.23	21.7	34.0	0.27	0.28
Chester.....	41.3	42.3	2.4	0.35	0.41	20.3	20.0	0.30	0.32
Hagerstown.....	39.5	47.1	19.2	0.60	0.60	23.0	23.0	0.53	0.71
Sassafras.....	37.2	51.3	37.7	0.27	0.26	13.3	24.7	0.19	0.21
Colts Neck.....	36.4	37.1	1.9	0.24	0.27	31.3	21.7	0.18	0.21
Sassafras.....	29.1	37.5	28.8	0.24	0.26	21.0	30.3	0.15	0.21
Lakewood.....	20.4	26.6	30.4	0.29	0.36	13.0	23.7	0.15	0.20
Sassafras.....	18.7	13.4‡	-28.3	0.32	0.37	12.3	7.0	0.13	0.23

\* The soils are arranged in the same order in all tables. This order was determined by the crop-producing power of the soils without the use of Mg, when all other factors were at an intended optimum.

† 2-Mg indicates 187 mgm. Mg added per pot, or 80 pounds MgO per acre, and 0-Mg indicates none was added.

‡ Some unknown factor or factors were responsible for the low results on these pots.

The amount of exchange Mg in the soil at the end of the experiment was generally lower than at the start for both the 0-Mg and the 2-Mg series. The Mg remaining in the soil of the 2-Mg series, however, was generally between 0.1 and 0.2 m.e. per 100 gm. higher than that in the 0-Mg series.

The most significant fact revealed by the data was the relationship between the amounts of Mg and K in the alfalfa plants (table 3). The average amount of Mg in the first crop for the 20 soils on the 0-Mg series was 23 m.e. per 100 gm. dry matter, as against 31 m.e. in the eighth crop. On the 2-Mg series,

the Mg values were 27 and 40 m.e., respectively. In contrast, the average amount of K in the first crop of the 2-Mg series was 55 m.e. and only 25 m.e. in the eighth. In other words, the Mg content of the eighth crop of alfalfa was greatly increased over that of the first crop, whereas its K content was greatly decreased.

In two previous papers (1, 2) it was pointed out that the K content of successive crops of alfalfa drops until the critical level<sup>6</sup> is reached, at which

TABLE 3  
*Mg and K and their ratios in alfalfa in specified series of tests and crops*  
In milliequivalents per 100 gm. dry matter

SOIL	FIRST CROP				EIGHTH CROP			
	0-Mg*	2-Mg			0-Mg*	2-Mg		
	Mg	Mg	K	Mg/K	Mg	Mg	K	Mg/K
Collington.....	18	31	60	0.5	30	37	30	1.2
Dover.....	30	34	60	0.6	53	57	19	3.0
Hoosic.....	23	21	57	0.4	38	39	23	1.7
Lansdale.....	16	21	59	0.4	22	26	30	0.9
Washington.....	22	29	52	0.6	25	36	19	1.9
Dutchess.....	30	25	51	0.5	36	39	29	1.3
Penn.....	20	19	53	0.4	15	23	31	0.7
Whippany.....	21	24	38	0.6	59	60	13	4.4
Gloucester.....	23	36	57	0.6	40	40	24	1.7
Bermudian.....	25	28	52	0.5	44	52	22	2.4
Papakating.....	21	26	44	0.6	30	39	18	2.2
Fox.....	35	40	57	0.7	66	69	21	3.3
Merrimac.....	13	20	55	0.4	12	23	19	1.2
Chester.....	25	28	59	0.5	35	43	40	1.1
Hagerstown.....	43	35	51	0.7	40	70	20	3.5
Sassafras.....	19	25	49	0.5	15	28	18	1.6
Colts Neck.....	14	16	50	0.3	17	27	24	1.1
Sassafras.....	15	23	56	0.4	10	24	24	1.0
Lakewood.....	21	28	74	0.4	23	32	24	1.3
Sassafras.....	23	33	61	0.5	14	33	46	0.7
Mean.....	23	27	55	0.5	31	40	25	1.6

\* No determinations of K were made on the 0-Mg series.

point the yield rapidly falls off. As the percentage K in the plant decreases, the percentages Mg and Ca tend to increase. These elements can apparently be substituted for K so far as its general functions within the plant are concerned. The change in the Mg/K equivalent ratios in the successive crops on the 2-Mg series of this experiment further illustrates this point. Thus the average Mg/K ratio in the first crop was 0.5 and that in the eighth crop was 1.6. Notwithstanding the great variation in the Ca, Mg, and K contents of the crops

<sup>6</sup> 0.15 to 0.20 m.e. per 100 gm. dry matter.

growing on the several soils, the sum of the equivalents of these elements per unit of produce for any given harvest was virtually constant for all soils under standardized conditions for growth.

Estimates of the rate at which the reserve Mg of these soils moved into the exchange form are presented in table 4. The columns headed "Fixed by Soil"

TABLE 4

*Exchange Mg in soils at start and end of test,\* Mg removed by eight crops alfalfa, and Mg fixed or released by soils*

SOIL	DRY SOIL PER POT	0-Mg SERIES OF POTS				2-Mg SERIES OF POTS			
		Mg in original soils	Mg removed by crops†	Mg in soils at end	Mg fixed‡ by 1000 gm. soil	Mg in soils at start	Mg removed by crops‡	Mg in soils at end	Mg fixed‡ by 1000 gm. soil
	gm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
Collington.....	6311	860	283	553	-4	1048	294	721	-5
Dover.....	6810	2907	413	2275	-32	3095	367	2484	-36
Hoosic.....	7173	837	317	663	+20	1025	299	785	+8
Lansdale.....	6492	671	271	316	-13	859	222	458	-28
Washington.....	6674	593	271	390	-10	781	316	430	+5
Dutchess.....	6628	1088	359	774	+7	1276	343	967	+5
Penn.....	6810	894	252	406	-35	1082	278	265	-79
Whippany.....	6265	2293	357	1859	-12	2481	331	1882	-43
Gloucester.....	6901	755	230	334	-28	943	271	503	-24
Bermudian.....	6174	1599	301	1209	-14	1787	300	1299	-30
Papakating.....	6855	500	225	292	+2	688	277	325	-13
Fox ..	7082	2824	369	2601	+21	3012	398	2945	+47
Merrimac.....	6902	272	146	128	+0.3	460	207	366	+16
Chester.....	6810	2021	206	1491	-48	2209	237	1623	-51
Hagerstown.....	6265	3573	359	2941	-44	3761	446	3154	-26
Sassafras.....	7582	203	125	148	+9	391	185	295	+12
Colts Neck.....	7037	214	143	154	+12	402	146	197	-8
Sassafras.....	6901	101	102	109	+16	289	162	109	-3
Lakewood.....	7673	103	79	103	+10	291	143	168	+3
Sassafras.....	7446	91	76	72	+8	279	66	190	+3

\* Expressed as milligrams per pot of soil or the produce thereof.

† Tops and roots.

‡ Plus-values mean release.

show positive and negative values, indicating both release and fixation. The amount of Mg released or fixed by the exchange complex of the 20 soils was relatively small in comparison with the K values obtained in a similar study, but so also were the quantities of Mg applied to or naturally present in these soils. The Fox and Hoosic showed the greatest release of Mg in the 0-Mg series; and the Chester, Hagerstown, Penn, and Dover soils, the highest fixation values. Ten of the soils in the 0-Mg series released Mg, and ten fixed the element. Seven of the soils that released Mg contained less than 300 mgm. of exchange Mg each per pot at the start of the experiment. The soils that fixed



Mg contained relatively large amounts of the element in exchangeable form at the beginning of the test. The rate of release of reserve Mg from the soil was reduced and the degree of fixation increased by applications of Mg sulfate. This is shown in the generally smaller positive and larger negative values for the 2-Mg series of pots than for the 0-Mg series in the two columns headed "Fixed by Soil," in table 4.

In evaluating the data in tables 1 to 4, inclusive, for the purpose of classifying the A-horizons of the 20 soils in relation to their need for Mg in fertilizer form, four criteria were employed. These were the absolute yields without the addition of Mg, the response of the alfalfa when Mg was applied to the soil, the content of exchange Mg in the soils as they came from the field, and the extent to which their reserve Mg was released for plant use. On the basis of these

TABLE 5  
*Grouping of 20 New Jersey soils in relation to Mg needs\**

GREATEST	INTERMEDIATE	LEAST
Lakewood sand	Penn silt loam	Collington loam
Sassafras sand	Fox gravelly loam	Dutchess shale loam
Sassafras loamy sand	Colts Neck sandy loam	Bermudian silt loam
Sassafras loam	Washington loam	Whippany silty clay loam
Merrimac silt loam	Chester loam	Dover loam
Gloucester loam	Papakating stony loam	Lansdale loam
Hagerstown loam		Hoosic gravelly loam

\* The need of these soils for Mg is in the order shown, the one at the top of each column having the greatest need and the one at the bottom the least.

criteria, the 20 soils have been arranged in table 5 in the order of their need for Mg.

It is apparent that the rating for any given field of any one of these soil types might well be higher or lower than is indicated by the classification, depending upon the treatment it has received at the hands of the operator. The position of the Dutchess, Hoosic, Fox, and Hagerstown soils might have been entirely different if virgin samples of these soils had been studied. The ratings of all 20 soils are tentative and may have to be changed when further evidence has been accumulated.

#### SUPPLEMENTAL OBSERVATIONS

There is reason to believe that 80 pounds MgO per acre was not sufficient for optimum yields on the soils that contained the least exchange Mg. Thus the low-Mg soils occupied a much lower position in the scale of productivity in this test than in a previous similar test in which dolomitic limestone rather than  $\text{CaCO}_3$  was used for raising the pH values to the desired level. With dolomitic limestone the rate of application of MgO ranged between 1200 and 1500 pounds per acre on Sassafras loam and on the Merrimac and Colts Neck soils. Comparison of the earlier test with the one currently reported showed that the

Sassafras soil occupied the fourth place instead of the ninth in the list; the Merrimac, the eighth instead of the tenth; and the Colts Neck, the sixth instead of the seventeenth position.

A number of these soils fixed Mg. This fixed Mg, like fixed K, is probably not so unavailable to plants as that in the primary-mineral form. It constitutes a different type of reserve that becomes more and more readily available to the crop as the need for the element increases. As in the case of K the results suggest the existence of an equilibrium between exchangeable and fixed Mg. Thus fixation tended to occur with high Mg applications and release took place when little or no Mg was applied (4).

As in the K experiment, some unknown limiting factor or factors operated to prevent optimum growth in those soils that rated at the bottom of the list in productivity. It seems probable that the crop-growing potentialities of the sandier soils of this group would have been greatly increased by dividing the lime, fertilizer, and trace-element applications into small doses for use at regular intervals during the period of the test. The soils with the highest storage capacities tended to produce the highest yields.<sup>7</sup>

An examination of the cation content of the exchange complexes in these soils (table 1) reveals that a majority of those in which Mg constituted less than 10 per cent of the total responded to the use of additional amounts of this element. These data correlate well with the hypothesis set forth in a previous publication (3) in which the possibility of ideal ratios of Ca, Mg, and K in the exchange complex was suggested. These ratios were tentatively set at 65 per cent Ca, 10 per cent Mg, and 5 per cent K, the remaining 20 per cent being allotted to H.

The portion of the applied Mg that was recovered in the harvested crops and in the roots varied between 0 and 46 per cent, the highest recovery being obtained from Hagerstown loam, a soil that was very high in both total and exchange Mg. In general, the greater the need for extra Mg, the larger the percentage recovery of that applied.

The Mg/K ratio in the exchange complex of these soils was much higher at the end of the test than at the beginning.

#### CONCLUSIONS

No correlation exists between the total Mg in soils and their crop-producing powers.

The most important single factor influencing the Mg uptake of plants is the quantity of K that is available for their use. If an abundance of K is at the plant's disposal, its content of Mg will be relatively low. As the K supply decreases with repeated harvests of a crop like alfalfa, the Mg content of the plant increases, even when the plant is growing on a soil that is very deficient in Mg. This would indicate the advisability of using additional Mg in proportion as larger amounts of K are applied to the soil.

<sup>7</sup> A third series of studies designed to obtain more information on what these limiting factors are and how they can best be overcome is now under way.

Response to Mg additions is governed in part by its ratio to the other cations in the exchange complex, particularly those of Ca and K.

It is doubtful whether 80 pounds available MgO per ton of fertilizer is adequate to meet the needs of crops where high-K fertilizers are applied to soils that are low in exchange Mg. Thus when, in a previous test, some of the same Mg-deficient soils were treated with dolomitic limestone in amounts supplying up to 1500 pounds MgO per acre they were relatively much more productive than in this test in which  $\text{CaCO}_3$  was used to raise the pH values and only 80 pounds MgO was applied as the sulfate.

If Mg constitutes less than 6 per cent of the exchange cations in a soil, crops growing on that soil are likely to respond markedly to applications of the element in soluble form. The ideal amount of Mg is believed to be about 10 per cent of the total exchange capacity of the soil.

Mg fixation occurred in about half the soils used in this study.

Of the 20 New Jersey soils studied, those of the Sassafra, Lakewood, Merri-mac, Gloucester, and Penn series had the greatest need for Mg, and those of the Bermudian, Whippany, Dover, Lansdale, and Hoosic series, the least.

Hagerstown loam was an exception to the general rule in that, even though 27.6 per cent of its exchange capacity was taken up by Mg, the yield of alfalfa on that soil was markedly increased by an application of magnesium sulfate.

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# THE FORMS AND REACTIONS OF MANGANESE IN THE SOIL

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The chemistry of manganese in the soil is of interest for at least three reasons: First, on some neutral and alkaline soils, manganese is insufficiently available to plants for healthy growth; second, on some acid soils plants absorb it in toxic amounts; third, the distribution of the various forms of the element in the soil is closely connected with the processes of soil formation. The chemical discussion which follows relates to all these subjects, especially to the low availability of manganese on certain soils.

Manganese-deficiency diseases have been recorded for many crops in the field. The most important of these is oats, some varieties of which are so sensitive to deficiency that the plant dies without producing any grain. The symptoms of manganese deficiency in oats are very characteristic, and have led to the common name "gray-speck disease." Peas are less sensitive, but when the supply of manganese is inadequate they develop a peculiar trouble called "marsh spot," after its occurrence at Romney Marsh in England (9, 26). The trouble consists of the development of brown necrotic spots in the center of the seed, which may form even when the yield of the crop is normal. Laboratory studies of soils of low supplying power — hereafter called "deficient soils" — have been mainly associated with these two diseases.

Deficient soils, with minor exceptions to be dealt with later, have a pH value (measured in suspension in water) of at least 6.5 and usually over 7.0. The total manganese is irrelevant; it may range from 0.1 per cent down to a few parts per million. The deficiency, whatever the crop, may be treated in the field by lowering the pH of the soil to about 6, by adding a compound of manganese to the soil, or by spraying or injecting the affected plants with a manganese compound (27). It may also be treated in a pot by waterlogging the pot for 4 weeks and then restoring drainage, and also by sterilizing the soil with formalin or by heat. Organic compounds, including both quinol (32, 36) and quinone (36), have also cured the deficiency as soon as their first toxic effects have passed away. Not all these treatments are always successful, but each of them has had complete success on certain soils. All these facts have to be considered when attempting a chemical explanation of deficiency disease.

## PREVIOUS POT AND PLOT EXPERIMENTS

The writer has published some comparisons (12, 13) of different treatments on deficient soils. Since these reports are not accessible to many readers of this journal, the main results are here summarized and brought up to date.

Plot tests were carried out on a gray sandy loam containing about 3 per cent organic matter ("University soil") which had been heavily limed to about pH 7.4

and on which cereals suffered acutely from manganese deficiency. The best results were always obtained by acidification with sulfur; the next best treatment was to sow the seed with crystalline manganese sulfate (100 pounds per acre); and good results were also obtained by spraying plants with 1 per cent  $\text{MnSO}_4$  as soon as signs of deficiency appeared. Though this last treatment removed the symptoms, it resulted in lower yield of grain than the other treatments, since the primordia had already been damaged before the spray was supplied. Other treatments were a dressing of dried blood, which had no effect, and alkalization with caustic soda to above pH 8.5, which improved the growth of oats in some years without making them really healthy. Ammonium sulfate at the rate of 2 hundredweights per acre improved early growth, but gave a poor yield of grain, being too feeble an acidifying agent to cure the disease.

The residual effect of dressings of  $\text{MnSO}_4$  is also interesting. Heavy applications (4 hundredweights of the hydrate per acre) prevented the deficiency from appearing on wheat in later years, but had little residual effect on oats.

Other soils were tested in pots 36 inches high and holding about 25 kgm. soil. A calcareous sandy loam from Mount Gambier, an immature soil derived from volcanic tuff, was successfully tested by uniformly mixing 80 p.p.m. of manganese as  $\text{MnSO}_4$  throughout the pot and also by mixing the same amount of manganese as freshly prepared  $\text{MnO}_2$ , made by adding  $\text{KMnO}_4$  to a strong solution of  $\text{MnSO}_4$  and washing the precipitate thoroughly with dilute acid and water. These treatments remained effective for 8 years. During this time slight symptoms of deficiency occasionally appeared on the  $\text{MnO}_2$  pot, which, however, produced good crops of oats while control pots failed to produce any grain. Not until 10 years after application, during a dry spring, did severe gray-speck occur on both these pots. Reversion to a less available form on this soil is evidently slow. The most striking experiment with this soil consisted of waterlogging two pots for 4 weeks and then restoring normal drainage. Oats have made excellent growth on each of these, the effect having lasted now for 11 years. Acidification is also successful with this soil, though it is naturally too calcareous for this treatment to be practicable in the field. Similar results to these were obtained with a poor gravelly soil (Tinkurrin gravelly sand) from the Western Australian wheat belt. Another deficient soil, a black self-mulching clay of pH 6.8 from Penola, a reclaimed swamp in South Australia, was also cured by an application of 3 gm. of synthetic  $\text{MnO}_2$ , which has been effective for 7 years. Experiments on the soils of Mount Gambier and Penola were reported by Piper (25) in one of the first general discussions of the problem.

The question arises: Why is the residual effect with oats so poor on the University soil and so good on the other types? Both good and poor residual effects occur in the field. On the calcareous sandy loam at Corny Point, South Australia, where barley is sown with mixed superphosphate and manganese sulfate, responses to manganese have fallen off after 4 years of application. On the other hand, Townsend and Wedgworth (39), working with French beans on a burnt peat, reported a negligible residual effect in the next season after a heavy dressing of  $\text{MnSO}_4$ ; many similar results have been reported (33). In

fact, in some cases, as where fruit trees grow on deficient calcareous soil (27) no attempt is made to treat the soil, but  $\text{MnSO}_4$  is injected into the trunk.

#### CHEMISTRY OF MANGANESE IN THE SOIL

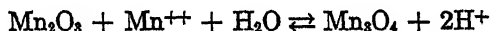
In the first place we can divide the manganese in the soil into the bivalent ion — existing in the soil solution or as an exchangeable ion or in a nonexchangeable form — and the insoluble higher oxides. All forms are in dynamic equilibrium with one another. At all pH values above 5.5, soil organisms can oxidize the bivalent form (14); this oxidation is rapid in well-aerated soils, especially in the pH range of 6.0 to 7.5. The reverse action also occurs. The higher oxides are reduced, whether by direct reaction with organic matter or by biological processes. Reduction by organic matter is more likely at low pH values, since the oxidizing power of the higher oxides increases rapidly with acidity. Biological reduction can take place at any pH value if the oxygen tension is low, when the anaerobic bacteria use the higher oxides as a source of oxygen. A long period of waterlogging at a high temperature can liberate large amounts of soluble manganese (25). If severe waterlogging is excluded, the bivalent form is favored in strongly acid soils, since bacterial oxidation is very slow or absent, whereas organic matter can reduce the higher oxides; again, the bivalent form is almost all removed from neutral or alkaline soils, since bacterial oxidation is rapid, and reduction by organic matter is now very slow; and in moderately acid soils the bivalent form diminishes with rising pH, since bacterial oxidation rises to a maximum while reduction by organic matter steadily decreases in importance.

#### *Higher oxides of manganese*

Since all but a minute fraction of the manganese in neutral and slightly alkaline soils is converted to higher oxides, these deserve more detailed attention than they normally receive. Their degree of reactivity is their most important distinguishing mark; their empirical chemical formulas are of minor importance. Most writers assume the composition  $\text{MnO}_2$ . Compounds approximating this formula undoubtedly occur in soil, though Naftel (19) has given analytical evidence for the formula  $\text{Mn}_2\text{O}_3$  in several soils. Recent fundamental work (20) shows how the composition of the test-tube autoxidation product is affected by the reactions



and



These reactions must occur in soils, but this aspect of the problem will not be pursued here for lack of evidence. The terms "manganic oxides" and "higher oxides" will be used to include all formulas from  $\text{Mn}_3\text{O}_4$  to  $\text{MnO}_2$ .

*Degree of reactivity.* D'Agostino (3) made a thorough study of the relative activities of different forms of  $\text{MnO}_2$ , both natural and synthetic, in order to estimate their value as depolarizers in dry cells. His method was to determine

the rate at which  $\text{CO}_2$  was evolved from a mixture of the sample with sulfuric and oxalic acids at room temperature. The most active form, synthesized by heating basic manganous carbonate to  $360^\circ\text{C}$ . in air, produced  $\text{CO}_2$  over 100 times as rapidly as did an inert natural pyrolusite. Great differences in activity also occur in soils. D'Agostino's method cannot work here, but instead we can use strong or weak reducing agents in solutions ranging from neutral to highly acidic. In this way we can extract the most reactive manganic oxide from a soil by a short treatment with a gentle reagent, such as a cold neutral solution of quinol. The same soil may also contain inert oxide which will not dissolve within a reasonable time unless it is treated with hot strong acid plus a reducing agent. Possibly the inert form might react with the gentler reagent if it could be given enough time; but the *rate* of reaction is the essential point here.

*Highly reactive manganic oxide.* It has been known for many years that some soils contain a highly reactive form of manganic oxide, which is reduced by quinol within 15 seconds, liberating alkaline  $\text{Mn}(\text{OH})_2$  and thus making it impos-

TABLE 1  
*Manganese extracted from soil by ammonium acetate and quinol after different contact periods*

SOIL*	Mn EXTRACTED	
	After 1 hour	After 6 hours
	p.p.m.	p.p.m.
A	10	21
B	26	29
C	41	68

\* All samples are from pots of Mt. Gambier soil. A is untreated and deficient; B has been much improved by adding  $\text{MnO}_2$ ; C was waterlogged 10 years previously and is free from deficiency.

sible to measure the pH of these soils with the quinhydrone electrode. This highly reactive form can be estimated by extracting the soil with quinol in a neutral solution of ammonium acetate or some other salt. Gisiger, in a valuable study of this reaction (8), found that one such soil liberated 181 p.p.m. Mn within 3 minutes of its mixture with quinhydrone and ammonium acetate — that is, during the time taken to filter the mixture. The time of this extraction should be standardized, and should preferably be no more than half an hour; longer periods, such as the 7 hours originally suggested (12), allow the less vigorous manganic oxides to dissolve, and so obscure the contrast between these and the most active form (see table 1).

This reactive form may also be roughly estimated in two other ways, which are useful as qualitative tests. The first depends on its ability to oxidize a benzidine salt in neutral solution to give a brilliant blue cation, which is strongly absorbed and colors the whole soil blue. The second is the catalytic destruction of  $\text{H}_2\text{O}_2$ , which can be followed either by the rise of temperature (1) or by the rate of evolution of oxygen (28). These tests, though valuable, are too complex

to be made quantitative. In particular, the depth of the blue color with benzidine depends on the adsorbing properties of the soil.

*Less active forms.* We may define the second-class manganic oxide as that which reacts with hyposulfite at pH 7, but not with quinol. We might also use the familiar fact that manganic oxide of whatever class becomes more susceptible to attack by common reducing agents as the pH falls. Thus, a moderately active fraction might be defined as that dissolved by quinol in 0.05 *N* H<sub>2</sub>SO<sub>4</sub>, but not at pH 7. This fraction overlaps that just mentioned; neutral hyposulfite is a more generally useful reagent, however, since it can be applied to calcareous soils (see table 2). The widespread occurrence of moderately active higher oxide is shown by the number of soils which can be tested by the quinhydrone electrode in aqueous suspension, but not in 0.1 *N* H<sub>2</sub>SO<sub>4</sub> (23).

TABLE 2

*Manganese leached from soil at pH 7 by 25 parts of normal ammonium acetate with and without reducing agents; showing the most reactive (dissolved by quinol) and the moderately reactive higher oxide (dissolved by hyposulfite)\**

soil†			Mn dissolved		
Origin	Condition	pH	No reduc- ing agent	+ 0.2% quinol	+ 0.4% Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>
			p.p.m.	p.p.m.	p.p.m.
Mt. Gambier.....	Mn-deficient	7.4	1.8	20	125
Mt. Gambier, 2 months after waterlogging.....	Healthy	7.4	17	111	...
Penola.....	Mn-deficient	6.8	0.0	0.4	0.4
University..	Mn-deficient	7.3	1.3	28	46
Corny Point.....	Mn-deficient	8.0	2.6	8	17
Werribee.....	Healthy	7.8	0.2	290	520
Dooen.....	Healthy	7.3	0.0	137	...

\* Some of the figures in this table are assembled from a previous article (12).

† The Mt. Gambier, Penola, and University soils are described in the text. The Corny Point soil is a highly calcareous sand; Werribee and Dooen soils are black friable clays, somewhat calcareous.

The rest of the manganic oxide, which requires more drastic treatment for its solution, may be regarded as inert.

#### *Exchangeable manganese*

Exchangeable manganese has usually been determined by extraction with neutral ammonium acetate, but Steenbjerg (35, 36, 37, 38) and Heintze (9) have used calcium nitrate or magnesium nitrate as extracting agents. Ammonium acetate has the great analytical advantage that it can be completely destroyed and the extracted manganese can then be easily determined colorimetrically with periodate as the oxidizing agent. A thick syrup of calcium or magnesium nitrate, on the other hand, is an awkward material in which to search for a few micrograms of manganese. However, Steenbjerg, working with



heavily limed podzols in Denmark, found that 0.5 *M* magnesium nitrate was the most effective extracting agent for manganese; calcium nitrate came very close to it, but ammonium and sodium salts were much less effective (see table 3). The contrast is confined to neutral and alkaline salts. As one extreme case, Steenbjerg (38) found a humic sand of pH 7.6 which yielded 0.0 p.p.m. of manganese to *N* NaNO<sub>3</sub> and 2.8 p.p.m. to 0.5 *M* Mg(NO<sub>3</sub>)<sub>2</sub>. The term "exchangeable" evidently means little unless the replacing ion is defined.

A further analytical difficulty reported by Sherman and Harmer (32) is that some soils release larger amounts of exchangeable manganese if they are air-dried before extraction. The same observation has been made in this laboratory.

### *Dilute acid extracts*

Dilute acids have sometimes been used as reagents for exchangeable Mn. Hydrogen ion is certainly much stronger than ammonium in its ability to displace adsorbed manganous ion, and Steenbjerg (37, p. 805) asserted that it released man-

TABLE 3

*Manganese extracted, by nitrates of various cations, from humic sand at Borris after addition of various amounts of calcium carbonate\**

CaCO <sub>3</sub> ADDED PER HECTARE	pH	Mn EXTRACTED†				
		NaNO <sub>3</sub>	KNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>
kgm.		p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
2000	5.8	13.0	12.1	13.0	18.2	17.8
8000	6.5	2.9	2.9	3.0	9.3	7.6
16000	7.2	0.7	0.7	0.7	5.3	4.4

\* From Steenbjerg (35, p. 429).

† Extracting solutions, molar in nitrate ion.

gane more than twice as efficiently as did magnesium. The use of dilute acids for this purpose is an unsound practice, since an acid also dissolves some higher oxide which is reduced by the humus at a low pH. In fact, the amount of Mn dissolved may depend less on the Mn compounds in the soil than on the amount and activity of the humus in the soil! Thus, if excess of synthetic MnO<sub>2</sub> is added to 0.5 gm. of Penola soil (rich in humus, poor in MnO<sub>2</sub>) and also to 0.5 gm. of an alkaline soil from semiarid Victoria (poor in humus, rich in MnO<sub>2</sub>), and each is shaken for 30 minutes with 100 ml. of 0.05 *N* H<sub>2</sub>SO<sub>4</sub>, the former dissolves 0.3 mgm. Mn and the latter 0.05 mgm. The same reduction was shown by Sen-Gupta (29), who found that soil left in contact with dilute H<sub>2</sub>SO<sub>4</sub> lost its power to oxidize phenol — that is, the most active MnO<sub>2</sub> was slowly destroyed by the organic matter of the soil. Ammonium chloride, being an acidic solution, may give too high figures for exchangeable Mn in the same way as do dilute acids. Dilute acid extracts may give useful information, however, as they include both exchangeable Mn and some of the most reactive higher oxide, and so allow for an estimate both of the most active manganese in a natural

soil and also of the amount of toxic manganese that may come into solution in an acid soil, as in McCool's work (16). A further possibility is that dilute acid liberates some manganese from  $Mn_2O_3$  but not from  $MnO_2$  (20).

#### *Fate of $MnSO_4$ in the soil*

When the manganous ion is added to a neutral or alkaline soil it is turned into the exchangeable ion and becomes mostly insoluble in water. From this state it is slowly oxidized by bacteria to a higher oxide, the process taking 3 or 4 days, or more if the temperature is not uniformly as high as 25°C. Nonbiological oxidation is probably negligible in the majority of soils of pH below 8; its importance was overemphasized in the author's earlier work (12). This is shown by the very fact that bacteria form a ring of higher oxides in soil-agar plaques in the less alkaline range when manganese is supplied as a central plug of  $MnSO_4$ -agar (7, 14, 17); during the several days needed for this process the manganese must have diffused as the bivalent ion. Sherman *et al.* (31, 32), however, have expressed the opposite opinion, and the results of Wain *et al.* (41) are similar to theirs. They have found that when  $MnSO_4$  is mixed with certain neutral or alkaline soils in the normal range of field moisture, the manganese is almost entirely converted into a form insoluble in neutral ammonium acetate, at a rate far too rapid for bacteria to be involved. This change is even recorded within 3 hours of mixing. They attribute this change to oxidation, since about half the added manganese could be extracted with quinol. However, none of the soils tested in this laboratory, neutral or alkaline, deficient or healthy, have given any evidence of a disappearance of exchangeable manganese within 6 hours of the addition of  $MnSO_4$ . Ammonium acetate may extract as little as one fourth, but calcium nitrate extracts more than half of the added Mn in a single shaking of 1 part of soil to 10 parts of salt solution. Steenbjerg (36, p. 359) found that two deficient alkaline soils released 20 to 30 per cent of added Mn when shaken with sodium nitrate 2½ hours after mixing, and his results agree fairly well with those obtained here, in view of the low extracting power of sodium. This discrepancy between different workers clearly needs more study.

The amount of exchangeable Mn in any soil varies through the seasons. This is shown by Sherman and Harmer (32) and especially by Steenbjerg's figures (36, 37), which are by far the most comprehensive on this subject. A series of plots were tested in 1931, a wet year in Denmark, and in 1934, a dry year. Results on two representative plots are quoted in table 4. The difference between limed plots and controls falls off with time; this must be a seasonal effect. The limed plots also are lower in exchangeable Mn in 1934, but this may be due not only to the season but to a permanent change from manganous to manganic as a long-term result of the liming in 1931. The exchangeable Mn on both the University plots and the Mount Gambier pots also varies greatly through the seasons.

Though there is ample evidence of the conversion of bivalent manganese to higher oxides in the field, there is little direct evidence of any further aging to

inert forms. The fact that such inert forms exist in nature shows that this aging must occur; its speed undoubtedly varies greatly among different soils.

#### AVAILABILITY OF MANGANESE

##### *Bivalent manganese*

Some workers regard the bivalent ion as available and the higher oxides as unavailable. They therefore try to estimate the available manganese by extracting the soil with a neutral salt. Using magnesium nitrate, Steenbjerg drew the line of sufficiency at 2 p.p.m. of exchangeable manganese; above this figure, oats were usually healthy, below it they suffered from gray-speck. The separation is not at all clean; sick soils were found with more than 2 p.p.m. and healthy soils with less than 1 p.p.m. Later (38) he raised the dividing line to 3 p.p.m. The seasonal variation in exchangeable Mn is great enough to create a further difficulty. Heintze (9), studying soils of Romney Marsh on which peas

TABLE 4

*Manganese extracted from two soils, limed and unlimed, by 0.5 M magnesium nitrate\**

CLAY, DOVER				SAND, THOUGARDSLUND			
1931		1934		1931		1934	
pH	Mn	pH	Mn	pH	Mn	pH	Mn
	<i>p.p.m.</i>		<i>p.p.m.</i>		<i>p.p.m.</i>		<i>p.p.m.</i>
5.7	88	6.2	8.4	5.7	3.8	5.4	2.1
6.1	51	6.3	7.3	6.4	1.6	6.2	0.6
6.8	30	6.9	4.4	7.2	0.8	7.5	0.2
7.5	8	7.7	1.6	7.7	0.5	8.0	0.0

\* From Steenbjerg (36). Each soil was treated with calcium carbonate at three different rates. The first line gives the values for the untreated soil, the other treatments follow in increasing order of heaviness of application.

developed marsh-spot, found, in contradiction to Steenbjerg, that calcium nitrate dissolved more manganese than did magnesium nitrate; the ratio of her values, calcium-extracted to magnesium-extracted, ranged between 1 and 4. Her other results are also in striking conflict with Steenbjerg's. One soil with marsh-spot yielded 25 p.p.m. of manganese to calcium nitrate solution — a surprisingly high figure for any alkaline soil, let alone one with manganese deficiency!

If we omit the Romney Marsh soils as having some peculiar feature still to be revealed, it appears that we might draw a line for alkaline soils at about 3 p.p.m. of exchangeable Mn when a magnesium salt is used for extraction, or 2 p.p.m. when an ammonium salt is used, as sufficient to guard against deficiency disease. Unfortunately we cannot transform calcium or magnesium extracts to ammonium extracts by using a constant factor. Further, a few deficient soils contain more than 2 p.p.m. of Mn soluble in neutral ammonium acetate (30, p. 255; 40).

In nearly all these cases, a value which is marginal or low for a pH of 7 becomes satisfactory if the pH is lowered to 6.

*Available manganic oxide*

There remain, however, a great number of neutral or alkaline soils which contain much smaller amounts of exchangeable Mn than this and yet are not deficient. The suggestion (12) that these owe their health to active manganic oxide, which can be a satisfactory source of the element if present in large amounts, has been supported in America (30) and in England (40). Whether this manganic oxide can be used directly by roots or merely serves as a reserve of manganous ions for the soil solution, remains to be settled. Of the soils referred to in table 2, those with quinol-soluble manganic oxide greater than 100 p.p.m. Mn are healthy, whereas those with small amounts are deficient. The success of  $MnO_2$  on the Mount Gambier and Penola soils also favors this hypothesis. So does the lasting effect of a 4-week waterlogging of the Mount Gambier soil. This soil is remarkable for containing a large amount of manganese which is dissolved by hyposulfite but not by quinol and which, therefore, is not normally available. Apparently this store of Mn is reduced by the waterlogging and when eventually reoxidized is converted to a reactive higher oxide, which can supply the needs of the plant. Presumably, quinol and quinone have a similar lasting effect (36).

According to Gericke (6), a sample of basic slag which vigorously decomposed  $H_2O_2$  was effective against gray-speck of oats. The Mn in basic slag may vary considerably in its activity. Two samples tested in this laboratory, one of which was prepared in Germany, contained 4.5 per cent Mn, but yielded only 0.2 per cent Mn to a solution of quinol in 0.05 *N*  $H_2SO_4$ , and did not react markedly with cold  $H_2O_2$ .

The contrary belief, that  $MnO_2$  actually causes Mn deficiency, has been associated with Rothamsted Experimental Station (9) and was apparently based on Steenbjerg's failure (36) to obtain a complete cure with precipitated  $MnO_2$  as fertilizer on an alkaline sand high in humus — although it gave a ninefold increase in grain. This belief also relies on the autocatalytic nature of the microbial oxidation of manganous salts: once a colony of Mn-oxidizers is started, bivalent Mn ions from solution are adsorbed on the  $MnO_2$  and oxidized there. Though rapid oxidation of bivalent Mn ions must, however, lower the availability of the element, this argument has surely been overdone [*e.g.* (17)]; healthy soils can oxidize  $MnSO_4$  just as rapidly as deficient soils (14). If  $MnO_2$  were really harmful, it must follow that the more  $MnSO_4$  was added to a soil, the more deficient the soil would become.

The most substantial contribution to this subject is the work of Mulder (18, chap. 5), according to whom copper compounds stimulate the bacterial oxidation of manganese. This result has been used to explain the intensification of gray-speck on the addition of  $CuSO_4$ , which has been observed on peaty soils. Tests made in this laboratory, however, both with moist soils and with soil-agar plaques, showed that bacterial oxidation of  $MnSO_4$  was unaffected by  $CuSO_4$ . Sherman *et al.* (31) have asserted that copper compounds actually retard this oxidation and quoted experiments showing good effects of  $CuSO_4$  on a Mn-deficient

soil. Antagonism between copper and manganese appears, then, to be peculiar to individual soil types. Incidentally, one can hardly accept the antagonism of excess ferrous iron (34) as a likely cause of Mn deficiency in a well-drained alkaline soil in the field, whatever may be found in water cultures.

#### *Limitations of quinol extraction*

The hypothesis that active manganic oxide is a satisfactory source of Mn is supported by every example of a good residual effect of  $\text{MnSO}_4$  or  $\text{MnO}_2$ . Some observations, however, conflict with this hypothesis; some soils are rich in active  $\text{MnO}_2$  but fail to supply plants with normal amounts of Mn. The soils of Romney Marsh, already referred to as producing "marsh-spot," are an example. These contain high concentrations of both exchangeable Mn and active manganic oxide. Next there are the many soils on which residual effects are low. It should not take more than 50 pounds of Mn per acre (or 200 pounds  $\text{MnSO}_4$  crystals) to overcome deficiency, but this amount on some soils fails to have a permanent effect. The University soil itself presents a peculiar problem. Oats and canary-grass, *Phalaris minor* (which grows as a weed), develop acute gray-speck on this soil even on plots which now contain over 200 p.p.m. of residual quinol-soluble Mn. These facts are still to be explained. No analytical method has ever been suggested which can distinguish between healthy and deficient soils in the range pH 7 to 8 without admitting striking exceptions. Not only does deficiency disease develop on some soils which yield ample Mn to ammonium acetate and quinol, but it fails to show on other soils which are low in quinol-soluble Mn, such as that quoted by Sherman *et al.* (31, p. 1081) which produced healthy oats after heavy liming while its quinol-soluble Mn was 1.6 p.p.m. All that can be said for the author's suggested use of neutral quinol is that the number of exceptional cases becomes thereby much smaller than with the simple extraction with a neutral salt. The great majority of healthy neutral and alkaline soils contain over 100 p.p.m. of quinol-soluble Mn. Further, a good reserve of quinol-soluble Mn in an acid soil makes it unlikely that heavy liming will cause a deficiency.

Analyses for Mn in the leaf have been successfully used for diagnosing deficiency (27), but even they provide some exceptional cases. Though 15 p.p.m. is a reasonable dividing line between sick and healthy oat plants, sick plants have been reported with as much as 29 p.p.m. (17) and even 36 p.p.m. (31). The possibility of ever finding a universally valid chemical test is reduced by Gerretsen's demonstration (7) that plants grown on a medium low in Mn are healthy as long as the medium is kept sterile but are attacked by gray-speck disease when the bacteria from "deficient" soil are introduced. He first identified the good effect of formalin with this action. Finally, little attention has apparently been paid to Hiltner's observation (11) that plants given additional  $\text{CO}_2$  were free from disease. Possibly this and other complicating factors must be considered on certain soils.

#### *Acid deficient soils*

The vast majority of acid soils can supply ample Mn to plants, and some even supply an excess. Some, however, have been so severely leached that they too

have become deficient. The total Mn of these soils is low. Most recorded examples of Mn deficiency on acid soils are concerned with trees. This may be partly because the store of Mn is gradually locked up by a tree, and partly because many leached profiles have extremely poor supplies of Mn in the lower horizons, where the tree may be feeding. This seems to apply, for example, to the Norfolk series in Florida, where severe deficiency occurs at pH 5.8 (2). McCool (16) referred to a profile of Norfolk sandy loam containing only traces of Mn soluble in 0.2 *N* acetic acid below the first 12 inches. A particularly interesting case has been described from the coastal district of New South Wales north of Sydney. There, orange trees have less than 10 p.p.m. in their leaves and suffer from Mn deficiency when growing on a poor sand, of pH 4.5 to 5.0, derived from sandstone (15). Elsewhere on a similar soil type, beans accumulate 500 p.p.m. Mn, though the soil contains only 5 p.p.m. extractable by 0.2 *N* acetic acid (22). This is evidently highly available while it lasts, and is all the more readily exhausted. The rainfall in this district is 49 inches, with a summer-autumn maximum.

#### *Correlation of gray-speck and marsh-spot*

Little work has been published on the occurrence of gray-speck and marsh-spot on the same soil, though Pethybridge (24) was first led to suspect the connection of Mn with marsh-spot by observing gray-speck of oats nearby. In the present studies, severe marsh-spot was found with "Greenfeast" peas growing in each of three pots of Penola soil; it was absent from one pot which had been treated 5 years earlier with  $\text{MnO}_2$ . Peas grew luxuriantly on Mt. Gambier soil and were free from marsh-spot though oats can barely produce grain on this soil; possibly peas can use the hyposulfite-soluble reserve (see table 2). Peas suffered severely on the untreated University soil and died without producing seed. On plots treated with  $\text{MnSO}_4$  5 years previously, peas grew fairly well, but the seeds were severely affected with marsh-spot. On plots treated with  $\frac{1}{4}$  pound  $\text{MnO}_2$  per square yard in the year of the trial, the peas grew excellently and were free from marsh-spot, yet oats with the same treatment suffered acutely from gray-speck.

#### DISTRIBUTION OF MANGANESE IN PROFILES

The pedology of manganese has had surprisingly little attention in view of its close connection with the processes of soil formation.

At least eight factors are concerned in the distribution of manganese; namely, (a) the weathering of minerals or dead plants to liberate manganous ion; (b) downward movement of  $\text{Mn}^{++}$  in drainage water; (c) equilibrium between  $\text{Mn}^{++}$  in solution and as exchangeable cation attached to negative colloids, organic or inorganic; (d) uptake of  $\text{Mn}^{++}$  by roots, followed by its restoration in litter on the surface; (e) oxidation of  $\text{Mn}^{++}$  by oxygen to higher oxides, normally a bacterial action; (f) aging of manganic oxides from highly reactive to less reactive or inert forms; (g) reduction of manganic oxide to  $\text{Mn}^{++}$  by organic matter or by anaerobic bacteria; (h) direct absorption of manganic oxides by plants or microorganisms. The first four of these are shared by other metals, the last four are not.

*Total manganese*

There are several patterns of distribution of total Mn in a profile, of which the following are the commonest:

1. Surface accumulation, minimum in subsurface, then increase with depth. Various leached soils have this pattern, and probably many more would be found to have it if the surface horizon were separated into fractions. Manganese, like calcium, is often concentrated at the surface of leached soils through the action of plants.
2. Steady decrease with depth. This is also found in leached soils, especially in those with red tones.
3. Steady values throughout profile. Pedocals and unleached soils belong here.
4. Accumulation in the subsoil. Some types contain such a horizon, often just above a calcareous layer.

The place of factor (*d*) in producing surface accumulation has seldom been discussed. A flora producing a ton of dry matter per acre annually, containing 200 p.p.m. Mn (a modest figure for an acid soil), could accumulate 40 pounds per century if all the element were collected from lower layers and fixed in the surface layer. Since the surface soil would itself supply much of the plant's intake, however, it seems that this process cannot account for differences of two or three parts per thousand in total Mn between upper and lower horizons, though it may well account for the distribution of "active" Mn. Factor (*e*) has been shown by Drosdoff and Nikiforoff (4) to be of great importance in localizing concretions of higher oxides.

*Active manganese*

Not much information is available as to the distribution of active Mn in profiles—the term "active" being used to include exchangeable Mn plus that dissolved from higher oxides by neutral quinol or by dilute acetic acid. It appears that the patterns described for total Mn are reproduced for active Mn, but with much stronger contrasts between horizons. McCool (16), who was interested in the accumulation of toxic quantities of Mn in acid soils, determined the amounts extracted by 0.2 *N* acetic acid from several profiles. The typical leached soils show a high concentration of active Mn at the surface, with a sharp decrease in the subsoil. If a lower horizon is alkaline, the active Mn increases again with depth; otherwise it remains very low. The one pedocal in his collection (Scoby loam) is well supplied throughout with active Mn, no horizon having less than 48 p.p.m. An extreme case in surface concentration is his Orangeburg sandy loam, with 105 p.p.m. in the surface 2 inches (of pH 5.6) and only traces below this. The absence of reactive manganic oxide from leached subsoils may often be due to waterlogging followed by slow drainage, which would remove manganous ion and eventually leave behind only inert higher oxides which are not affected by waterlogging. This has evidently occurred in the Penola soil referred to earlier, which has been reclaimed from a swamp, and contains about 50 p.p.m. Mn, only 1 part of which is extractable by gentle reagents.

Gisiger (8) referred to profiles in which Mn is extracted with quinhydrone at

pH 7. These are neutral or alkaline and contain over 100 p.p.m. active Mn throughout. A profile near Adelaide, which is only slightly leached and contains  $\text{CaCO}_3$  in the  $B_2$  horizon, shows a similarly good supply (42), with every horizon exceeding 100 p.p.m., and over 400 p.p.m. in the top 4 inches.

Robinson (28) also studied several profiles showing zones of accumulation of active Mn either in the surface or in the subsoil. He was chiefly interested, however, in extreme cases where there were concretions as large as sand and rich in  $\text{MnO}_2$ . Active Mn in these profiles was closely related to total Mn and to pH. Sherman and his colleagues (31, 32) also quoted profile analyses that agree with the above results.

\* These analyses agree, for the most part, with the observation of Hendricks and Alexander (10) that the  $B_2$  horizons of kaolinitic soils give no reaction with

TABLE 5  
*Total and quinol-soluble manganese in two leached profiles of southern Victoria*

SOIL	DEPTH	TEXTURE AND COLOR	pH	TOTAL Mn	QUINOL-SOLUBLE* Mn	RATIO QUINOL-SOLUBLE Mn / TOTAL Mn
	<i>inches</i>			<i>p.p.m.</i>	<i>p.p.m.</i>	
Podzolized soil on silurian mud- stone	0-6	Gray loam	5.0	128	25	.20
	6-12	Gray clay loam	5.1	120	15	.13
	12-22	Grayish yellow clay	5.0	66	4.5	.07
	22-35	Yellow clay	5.3	39	1.1	.03
	35-48	Yellow clay with decom- posing rock	6.0	38	0.6	.02
Red loam on Eocene basalt	0-13	Brown clay loam	5.8	1970	554	.28
	13-23	Red-brown clay	5.6	1000	245	.24
	23-32	Red-brown clay	5.8	442	44	.10
	32-48	Red clay	5.7	252	12	.03

\* The quinol-soluble manganese was determined by 6 hours' leaching with 0.5 M calcium nitrate solution containing 0.2 per cent quinol.

benzidine salts, whereas those of montmorillonitic soils give a strong blue color. Kaolinite is associated with low pH and leaching; mobile manganese in such soils is quickly absorbed by roots or removed in drainage. Montmorillonite persists in neutral or alkaline reactions where leaching is not intense, that is, in those environments where active manganic oxide can accumulate. Because of this coincidence, a positive reaction with benzidine is a good indication of montmorillonite. This rule also has exceptions; some red kaolinitic subsoils contain active oxides. The possibility that ferric compounds in the soil might also give a positive test (21) can be ruled out by dissolving the benzidine salt in ammonium acetate at pH 7, in which solution ferric compounds do not react. Benzidine, however, is not a general reagent for montmorillonite *clays* (5); it merely happens to react with many montmorillonitic *soil* horizons.



The rate of "aging" of active oxide into inert forms [factor ( $f$ ) in the foregoing list] must also be concerned in all these profiles, but all that can be inferred definitely is that it is not very rapid in pedocals.

McCool (16) also used another measure of active Mn in acid soils — namely, storing the moist soil at 72°F. or higher temperatures for a month, and then extracting the soil with water. He mentioned one soil that yielded 12 p.p.m. water-soluble Mn after a month at 100°F. This test is useful for highly acid soils which may accumulate toxic amounts of Mn by the interaction of organic matter and manganic oxide, but it does not apply if microbial oxidation is appreciable. In moderately acid soils the water-soluble Mn actually diminishes with time of storage.

The analyses given in table 5<sup>1</sup> are from the profiles of two representative types in the leached zone of southern Victoria. These show what appears to be the common pattern of a rapid decrease in active Mn with depth and a rapid decrease also in the ratio of active to total Mn.

#### SUMMARY AND CONCLUSIONS

The great majority of neutral and alkaline soils provide plants with adequate manganese. Most of these soils contain considerable amounts of reactive manganic oxide which can be extracted by a neutral solution of quinol. This solution gives a useful test of the ability of the soil to provide manganese. Some soils high in this reactive oxide, however, are associated with deficiency disease, while others with little extractable manganese are free from it. It seems that no single test can distinguish with certainty between healthy and deficient soils.

Figures for reactive manganic oxide in profiles are reviewed. The amount of this reactive oxide diminishes rapidly with depth in many leached soils.

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# DIFFERENTIAL THERMAL ANALYSIS OF HAWAIIAN SOILS<sup>1</sup>

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Although Hawaiian soils have been rather extensively studied, little is known about their clay or colloidal constituents. Hendricks and Fry (4), Kelley, Dore, and Brown (5), and others have demonstrated that the inorganic colloids of many soil types are largely crystalline. More recently, Kelley and Page (6) presented evidence which suggests that the colloidal material of certain soils from Hawaii and elsewhere contain considerable amounts of amorphous materials.

In this investigation the differential thermal method was applied to certain representative Hawaiian soils for the purpose of studying the kinds and amounts of crystalline materials present, special consideration being given to the distribution of the kaolin minerals in relation to soil-forming factors.

## QUALITATIVE AND QUANTITATIVE DETERMINATION OF KAOLINITE AND HALLOYSITE BY THE DIFFERENTIAL THERMAL METHOD

When the method of differential thermal analysis is applied to the minerals kaolinite and halloysite, there is a well-defined endothermic reaction at 500° to 600°C. This phenomenon apparently corresponds to the breaking of the crystal structure and the liberation of a definite quantity of water. It was suggested by Norton (7) that the magnitude of the displacement of the thermal curves corresponding to this reaction would be proportional to the concentration of mineral in a given mixture; others (1, 8) also have considered the area of displacement in relation to concentration.

The temperature at which the peak (maximum deflection of the differential galvanometer) of the endothermic reaction occurs is given by several investigators as 550° to 600°C. Increasing the heating rate tends to increase the temperature at which the peak occurs. Grim and Rowland (3) and Kelley and Page (6) suggest that the peak for halloysite occurs at a slightly lower temperature than that for kaolinite.

The differential thermal method was applied to dilutions of the kaolin minerals for the purpose of obtaining standards to aid in the qualitative and quantitative interpretation of thermal curves from kaolin-containing soils. Artificial mixtures

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or dilutions of kaolinite<sup>3</sup> and halloysite<sup>4</sup> with ignited aluminum oxide were prepared by placing appropriate amounts in an agate mortar and grinding until an intimate mixture of the two resulted. Tracings of the parts of the original differential thermal curves corresponding to the endothermic reactions for the various dilutions are given in figure 1. All curves were prepared by using the same weight of mixture uniformly packed into the heating block.

*Temperature of endothermic peaks in relation to dilution*

Figure 1 indicates that the dilution of kaolinite or halloysite affects the temperatures at which the endothermic peaks occur. The lower the concentration, the lower the temperature of the peak. For the same concentration the temperature for kaolinite is always about 20°C. higher than that for halloysite.

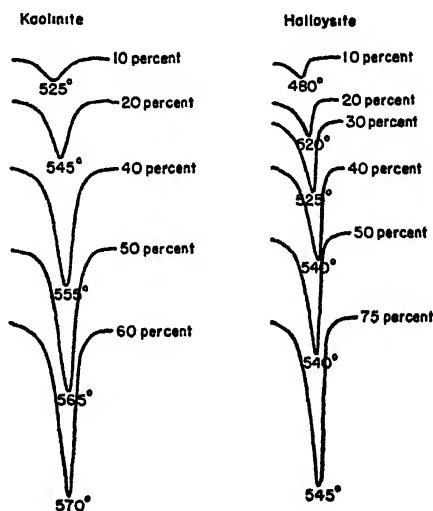


FIG. 1. ENDOTHERMIC PEAKS OF KAOLINITE AND HALLOYSITE IN RELATION TO DILUTION IN IGNITED ALUMINUM OXIDE

Thus, it did not appear probable that the temperature at which the endothermic peak occurs would be a satisfactory criterion to distinguish between kaolinite and halloysite in soils.

*Measurement of magnitude of the endothermic peaks*

The quantitative estimation of the amounts of kaolinite or halloysite from the magnitude of the endothermic peaks requires a satisfactory method for comparison with standard curves. Rough estimates can be arrived at by comparing an unknown curve with tracings of standard curves made on transparent paper. For a more refined method, however, the area or some other function of the displacement must be evaluated.

<sup>3</sup> Kaolinite, Langley, South Carolina.

<sup>4</sup> Halloysite, variety Indianaite.

In order to measure the area of the endothermic peaks it is necessary to establish the line of zero deflection and the point of departure therefrom. A study of numerous differential thermal curves including those from soils indicated that in many instances uncertainties will arise. The presence of organic substances and other unidentified materials is apparently responsible for the irregularities observed. Consequently, the trigonometric functions of the angle formed by extending the straight sides of the peaks was considered in relation to the concentration. For convenience, this angle is termed "angle  $\alpha$ " or "peak angle." Figure 2 illustrates the construction lines used in forming the peak angle. The general procedure is to lay a straight edge along the sides of the peak and extend the straight part of each side. Then the sine of this angle can rather

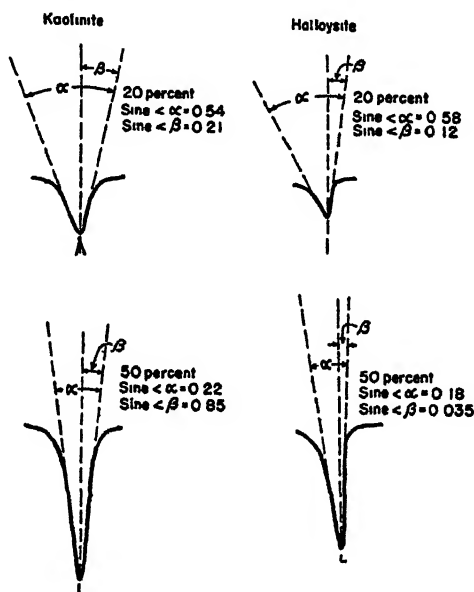


FIG. 2. CONSTRUCTION LINES FOR MEASURING ANGLE  $\alpha$  AND ANGLE  $\beta$

simply be determined by measuring 10 cm. from the vertex along the right-hand side and constructing a right triangle with a hypotenuse of 10 cm. The reciprocal of the sine, the cosecant, was found to be the most convenient function for expressing the magnitude of the peak angle.

Experience demonstrated that the trigonometric functions of the peak angles were a reliable measurement on which to base the magnitude of the endothermic effect of kaolinite and halloysite. When a trigonometric function of the peak angles for duplicate thermal curves of the same mixture were compared, excellent agreement was usually found.

In table 1 are given the cosecants of the peak angles and the ratios of concentration to cosecant of the peak angle for various dilutions of kaolinite and halloysite in ignited aluminum oxide. Since these ratios are nearly constant for

the range in concentration of 10 to 70 per cent, it is possible to assume that between these limits a linear relationship exists. The irregularities which do occur are attributed more to the difficulties of preparing uniform mixtures of two powders than to inaccuracies in the differential curves or their measurement. Also given in table 1 are the areas of the endothermic peaks and the ratios of concentration to area for the various dilutions of kaolinite and halloysite. The area measurements did not give so consistent a ratio with concentration as did the angle method. This was especially true of the halloysite mixtures. At corresponding concentrations, the areas of the peaks for kaolinite were considerably greater than those for halloysite. In an unknown sample, such as a soil, where it is difficult to distinguish between halloysite and kaolinite the area method would seemingly be less satisfactory than the method employing trigono-

TABLE 1

*Relationship of concentration of kaolinite or halloysite to the cosecant of the peak angle and the area of the endothermic peak*

CONCENTRATION	KAOLINITE				HALLOYSITE			
	Cosecant peak angle	Ratio Concentration Cosecant	Area of peak	Ratio Concentration Area	Cosecant peak angle	Ratio Concentration Cosecant	Area of peak	Ratio Concentration Area
<i>per cent</i>			<i>sq. cm.</i>				<i>sq. cm.</i>	
10	1.001	9.99	0.84	11.9	1.15	8.7	0.40	25.0
20	1.85	10.9	2.17	9.2	1.72	11.6	0.99	20.2
30	3.12	9.62	3.71	8.1	3.15	9.55	2.46	12.2
40	3.86	10.4	4.87	8.2	4.13	9.70	2.67	15.0
50	4.65	10.8	5.91	8.5	5.26	9.52	3.49	14.3
60	5.99	10.0	6.41	9.4				
68.75	6.80	10.1	7.12	9.6				
75	10.00	7.5			7.04	10.7	5.12	14.6

metric functions, since at the same concentration the peak angles for kaolinite and halloysite seem to be approximately of the same magnitude.

By changing the resistances in series with differential galvanometer, it is possible to extend the range of concentrations for which the above described quantitative measurements are adaptable.

#### *Shape of the endothermic peaks*

Figures 1 and 2 show a consistent difference in the shape of the endothermic peaks for kaolinite as compared with those for halloysite. The angle between the right-hand side of the peak angle and a perpendicular constructed to pass through the vertex (angle  $\beta$ , fig. 2) was always smaller for a given concentration of halloysite than for the corresponding concentration of kaolinite. Unfortunately only one variety each of kaolinite and of halloysite is represented, and it is possible that different varieties will give different-shaped endothermic peaks. Norton (7), for example, has shown that the particle size of kaolinite influences

the shape of the endothermic peak; the fine particles giving a smaller angle  $\beta$  than the coarser ones.

#### DISTRIBUTION OF KAOLINITE AND HALLOYSITE IN HAWAIIAN SOILS

##### *Materials and methods*

Soils from 20 selected locations in the Hawaiian Islands and two soils from Tahiti were utilized in this investigation. The factors which may have caused differences in the nature of the colloidal constituents of these soils are rainfall, maturity, and nature of parent material. The limits of rainfall from which soils were selected were 15 and 250 inches annually. The forms of parent material between which it is possibly significant to distinguish are (a) volcanic ash, porous, partly crystalline and partly glass in nature; (b) aa lava, a rough, rapidly cooled surface lava containing gas pores and frequently only partly crystalline; and (c) pahoehoe lava, smooth, slowly cooled lava, largely crystalline.

Differential thermal curves were obtained on all soil samples after they had been pretreated with hydrogen peroxide to remove most of the organic matter. The differences in the curves obtained from an untreated soil, an  $H_2O_2$ -treated soil, and the clay from an  $H_2O_2$ -treated soil are illustrated in figure 3. The soil organic matter apparently reflects its presence by a broad exothermic effect extending from 250° to 600°C.; this was almost completely eliminated by the hydrogen peroxide treatment. Comparison of the curve for the clay with that for the organic matter-free soil indicates that nothing was gained by making the clay separation.

The amounts of kaolin minerals in the soil samples were estimated from the differential thermal curves by using the equation: percentage of kaolin mineral = 10 cosecant of peak angle.

##### *Distribution of kaolin minerals in surface soils*

The differential thermal curves from the surface soils from Hawaii and Tahiti gave no indication that the surface soils contained clay minerals other than those of the kaolin type. This does not, however, preclude the possibility that soils from these areas might contain other clay minerals. Moreover, in 9 of the 22 soils examined, evidence that even the kaolin minerals exist is inconclusive. Estimates of the amounts of kaolin in the surface soils are listed in table 2. The amounts apparently varied from little or none to approximately 60 per cent.

For the purpose of discussion the soils were divided into the following groups according to their percentage of kaolin: 1. containing 20 per cent or more, 2. containing 5 to 20 per cent, and 3. containing less than 5 per cent. The soils in group 1 are all residual and come from areas of moderate rainfall, 20 to 90 inches. Presumably they were all developed from weathered basaltic lavas of the pahoehoe type. The soils placed in groups 2 and 3 come from a wide range of rainfalls, and there is no consistent source of parent material.

Why is it that the soils in groups 2 and 3 have such a low amount of kaolin? Is it because the kaolin minerals were not formed as the parent material



weathered or were they formed and then subsequently disappeared as a result of decomposition or deflocculation? Possibly the data (table 2) lend support to the hypothesis that in the weathering of porous, only partly crystalline materials such as volcanic ash and aa lava, under conditions of heavy rainfall the removal of certain of the products of decomposition is so rapid that there is little opportunity for the formation of the kaolin minerals, whereas under conditions of moderate rainfall there is a perceptible formation of kaolin minerals from these materials. On the other hand, in the less porous, compact lavas of the

TABLE 2  
*Estimated kaolin content of surface soils from the Hawaiian Islands and Tahiti*

GROUP	SOIL NO.	LOCATION	PARENT MATERIAL	RAIN- FALL	KAOLIN
				<i>inches</i>	<i>per cent</i>
1	41-148	Aiea, Oahu	Weathered basalt	50	63
1	39-481	Ewa, Oahu	Weathered basalt	20	57
1	37-491	Poamoho, Oahu	Weathered basalt	45	45
1	40-20a	Waimanalo, Oahu	Weathered basalt	90	31
1	40-17a	Nuuanu, Oahu	Weathered basalt	90	21
1	37-357a	Halemanu, Oahu	Weathered basalt	80	20
2	40-288	Makiki, Oahu	Aluvium	30	17
2	42-38a	Pensacola, Oahu	Volcanic ash	30	17
2	40-420a	Paauihau, Hawaii	Weathered basalt	65	14
2	42-22a	Aiea, Oahu	Volcanic ash	75	12
2	40-213a	Kona, Hawaii	Aa lava	70	10
2	38-349	Papara, Tahiti	Aluvium	100	10
2	41-147	Hilo, Hawaii	Volcanic ash	165	7
3	37-397a	Naalehu, Hawaii	Volcanic ash	45	<5
3	37-396a	South Point, Hawaii	Aeolin material	15	<5
3	41-165a	Honomu, Hawaii	Volcanic ash	250	<5
3	38-341	Haapape, Tahiti		65	<5
3	40-425a	Kaiwika, Hawaii	Volcanic ash	115	<5
3	41-150a	Kilauea, Kauai	Weathered basalt	65	<5
3	42-40a	Tantalus, Oahu	Volcanic ash	100	<5
3	40-423a	Hamakua, Hawaii	Volcanic ash	120	<5
3	40-437a	Olaa, Hawaii	Aa lava	170	<5

pahoehoe type the movement of water and products of decomposition is impeded and the conditions for the formation of kaolin are possibly more favorable.

It is rather difficult to explain certain of the properties of many of the soils in group 3. The differential thermal curves indicate the presence of almost no clay minerals, and in addition, some of the soils have almost no hydrous oxides. Yet these soils fix high amounts of phosphate, and certain of them have been shown by Ayres (2) to have relatively high inorganic base-exchange capacities. It is possible that some of the soils in group 3 contain alterations of the kaolin minerals and thus fail to give characteristic differential thermal curves. In

this connection it is of interest to examine the differential thermal curves from phosphated and unphosphated halloysite<sup>5</sup>, which had been ball-mill-ground for 9 days (fig. 4). These curves indicate that grinding reduced the typical

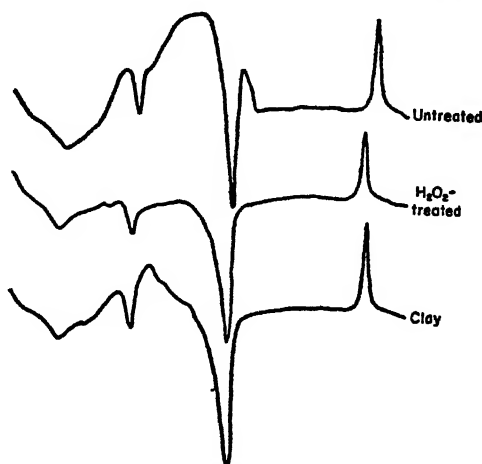


FIG. 3. COMPARISON OF DIFFERENTIAL THERMAL CURVES FROM AN UNTREATED SOIL, THE SAME SOIL AFTER HYDROGEN PEROXIDE TREATMENT, AND THE CLAY EXTRACTED FROM THE SOIL AFTER HYDROGEN PEROXIDE TREATMENT  
(Aiea soil No. 41-148)

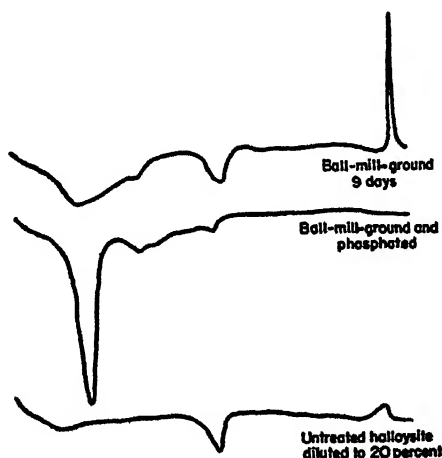


FIG. 4. EFFECT OF GRINDING AND PHOSPHATING ON DIFFERENTIAL THERMAL CURVES OF HALLOYSITE

endothermic effect by about 80 per cent, whereas the phosphated material gave almost no evidence of the presence of halloysite.

<sup>5</sup> These materials were prepared by P. R. Stout, Division of Plant Nutrition, University of California.

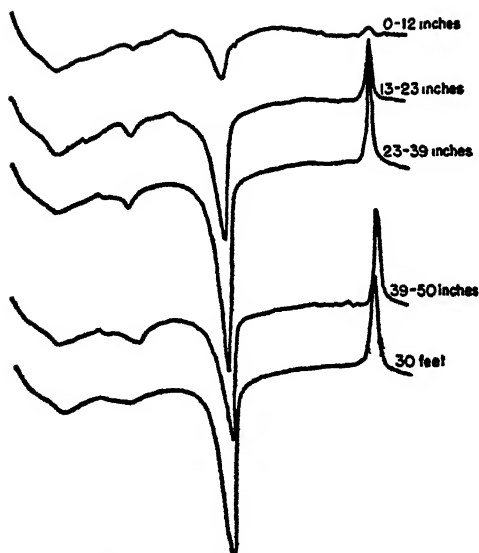


FIG. 5. DIFFERENTIAL THERMAL CURVES FROM A SOIL PROFILE, HALEMANU, OAHU  
(No. 37-357)

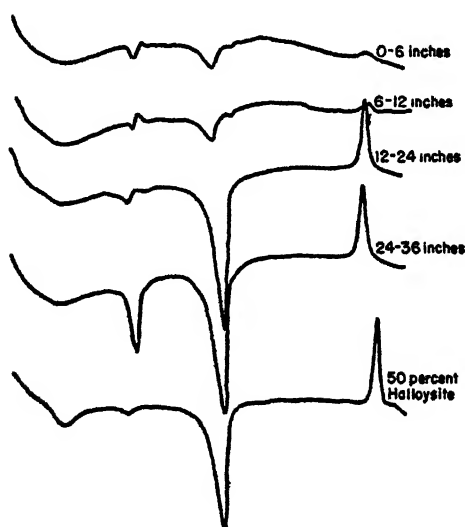


FIG. 6. DIFFERENTIAL THERMAL CURVES FROM A SOIL PROFILE, AIEA, OAHU (No. 42-22)

#### *Horizontal distribution of kaolin*

This study of the distribution of kaolin in Hawaiian soils also entailed a consideration of the vertical distribution in the various soil horizons. Figures 5 and 6 show differential thermal curves of relatively mature residual soil profiles presumably developed from weathered basaltic lavas of the pahoe-hoe type,

whereas figures 7 and 8 are from soil profiles developed from aa lava and volcanic ash, respectively.

The two soil profiles developed from pahoehoe lava (figs. 5 and 6) are similar in that the surface horizons are low in kaolin, while the parent material and other subsurface horizons are high. Of particular interest was the parent material of the soil profile from Halemanu. This material came from about 30 feet below

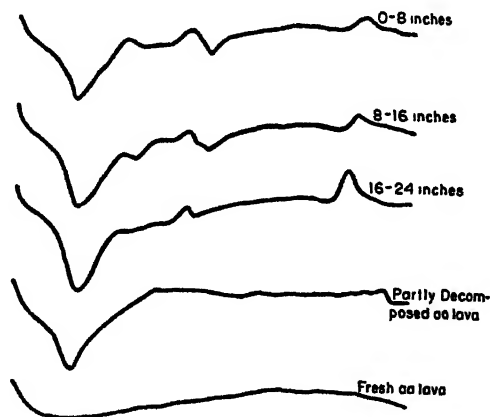


FIG. 7. DIFFERENTIAL THERMAL CURVES FROM A SOIL PROFILE, KONA, HAWAII (No. 40-213)

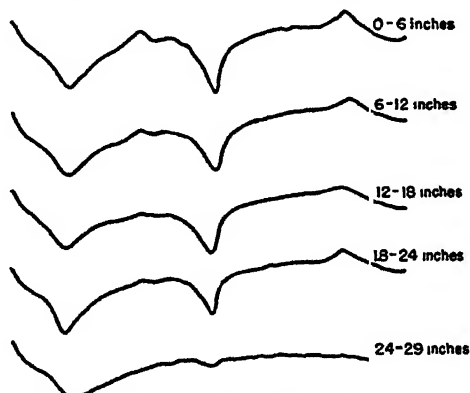


FIG. 8. DIFFERENTIAL THERMAL CURVES FROM A SOIL PROFILE, PENSACOLA, OAHU (No. 42-38)

the surface and apparently contains about 65 per cent kaolin. When this sample was collected it had all the appearances of unaltered rock; however, it was easily removed with a pick and when dried it crumbled readily. Apparently the formation of kaolin occurred early in the decomposition of this material.

Since the soils from Halemanu and Aiea (figs. 5 and 6) are residual in origin it seems likely that the low kaolin content of the surface horizons resulted either from the chemical decomposition of these minerals or from their deflocculation

and removal in colloidal suspension. Possible evidence of the latter appears in the Halemanu soil profile. The 23 to 39-inch horizon is appreciably higher in kaolin than the other horizons.

The soil profiles developed from volcanic ash and aa lava offer an interesting contrast to those just discussed. Here, the greatest amounts of kaolin are found in the surface soils. Profiles of this type are usually shallow and are considered relatively immature. In the Kona soil (fig. 7), the actual presence of kaolin could reasonably be doubted. The exothermic peaks are oddly shaped and are unusually large in proportion to the endothermic peaks. With the information now available it is not possible to decide why the parent material has not been rapidly kaolinized. Possibly age, mineralogical composition, and moisture relationships should be considered in this connection.

#### DISTRIBUTION OF HYDROUS OXIDES IN HAWAIIAN SOILS

It has been generally assumed that most Hawaiian soils contain abundant amounts of hydrated iron and aluminum oxides. This assumption has been based, for the most part, on their color and high phosphate-fixing capacity. However, the differential thermal curves for the 20 Hawaiian surface soils characteristically indicated the presence of only relatively small amounts of these oxides. In only two soils were high amounts of hydrous iron and aluminum oxides found to be present. These were from Kilauea, Kauai (41-150a) and from Kaiwika, Hawaii (40-425a). They probably contained about 40 per cent of a mixture of bauxite and goethite. There was no evidence that any of the other soils contained in excess of 10 per cent of these materials.

#### SUMMARY

This paper on differential thermal analysis as applied to Hawaiian soils gives consideration to: (a) the application of the method to the qualitative and quantitative estimation of halloysite and kaolinite, and (b) the distribution of kaolin in Hawaiian soils. The results may be summarized as follows:

The temperature at which the maximum endothermic effect for kaolinite and halloysite occurs depends upon the concentration or dilution of these materials.

The magnitude of the deflections caused by the endothermic effect is related to the concentration of material in a mixture, and trigonometric functions of the angle of the peaks are suggested as a means of evaluating this effect.

Only clay minerals of the kaolin type were identified in the surface soils examined, and the amounts present were found to vary from 0 to 60 per cent.

Apparently when lavas of the pahoehoe type are weathered, kaolin is readily formed, and the soils which are subsequently developed have lower amounts of kaolin in the surface than in the subsurface horizons.

Soils formed from volcanic ash and certain porous lavas are generally low in kaolin; the surface soils contain more than the subsoils.

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# DETERMINATION OF ELECTRICAL CONDUCTIVITY OF SOIL SOLUTION<sup>1</sup>

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The soils in the semiarid sections of the interior of British Columbia tend to be relatively high in their content of soluble salts. In many small spots throughout the farming and grazing areas, the soils are too saline for normal plant growth. The process of salinization has in many cases been aggravated by irrigation and by consequent seepage from above. An investigation is now under way into the soluble salt contents of soil samples from a wide area in the interior of the province. As a preliminary to this investigation, the use of an electrical resistance meter has been tested for determining the soluble salt content. This paper summarizes the findings with regard to the use of the resistance meter.

## REVIEW OF LITERATURE

Pioneer work on the use of an electrical resistance meter for determining the soluble salt content of soils was done by Davis and Bryan (5) in 1910. They found that the resistance of a soil extract bore a close relationship to the content of mixed soluble salts. The time required, after wetting, for the soil solution to reach equilibrium varied from 5 minutes to 25 minutes. Tables are given relating the salt content to the resistance readings at 60°F. In 1939, Gustafson and Behrman (8) concluded that the total salt content of a solution could be determined reasonably accurately by the conductivity procedure. They calculated factors to use for each type of solute. In 1943, Dunkle and Merkle (7) obtained a close positive correlation between the reciprocal ohms of a 1:2 extract and its soluble salt content. The regression line was straight. Merkle and Dunkle (13) reported similar results in 1944. With both mineral and organic salts present in the solution, they obtained the equation  $x = 206.3y - 0.01186$ , in which  $x$  = percentage of soluble salts and  $y$  = ohms  $\times 10^{-6}$ . The agreement was very close, and the use of the resistance meter was considered to be quite satisfactory for this purpose. Magistad and Christiansen (10) do not consider the conductivity procedure to be entirely accurate. They have expressed the belief that in studies of excess salt content, direct measurement of the osmotic pressure would be more reliable. Magistad and Reitemeier (9), however, found a close relationship between the electrical conductance and the osmotic pressure (determined by means of the freezing-point depression) of soil solutions. Magistad (11) pointed out that for routine field work the electrical conductance method is more convenient to use than the freezing point depression method.

The ratio of water to soil has received considerable attention. In 1924, Scofield (14) found that with successive dilution the salt content of the extract was reduced but the calculated soluble salt content of the soil was increased. He concluded that it was desirable to use a low ratio of water to soil. He obtained his extracts by displacement at the moisture-holding capacity and by centrifuging at the saturation point. In 1942, Anderson *et al.* (1) obtained more solutes from the soil with a 1:10 extract than with a 1:2 extract. In

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1945, Magistad *et al.* (12) obtained results similar to those of Scofield. For accurate results, they recommended extraction at a moisture content close to the moisture-holding capacity, using the displacement or the pressure-membrane method. For routine work, however, they suggested that a 1:1 ratio should prove satisfactory.

A number of workers have investigated the effects of filtering before taking electrical resistance readings. In most cases (10, 12, 13, 14), filtering has been recommended. In other cases (1), letting the soil-water mixture stand for a while and using the supernatant liquid has proved satisfactory. Magistad *et al.* (12) reported that the direct determination of resistance on a thick soil paste was not reliable.

The length of time to allow the soil and water mixture to stand before readings are taken has also received consideration. In 1942, Anderson *et al.* (1) found that after 24 hours the salt content of the extract increased. This was attributed largely to the action of micro-organisms, but partly to the slow solution of certain inorganic compounds in the soil. These results are in line with those reported at various times on the effects of time of standing on the contents of individual elements in the extracts. In actual practice, all the way from 20 minutes (5) to 24 hours (1, 14) has been used.

There has been some difference of opinion as to the best method of expressing the results of electrical resistance readings. Scofield (14) felt that the readings should always be expressed as parts per million of soluble salt content of the dry soil. Anderson *et al.* (1) also converted their data into parts per million of dry soil. For the most part, however, investigators appear to have preferred to express their results as reciprocal ohms (mhos)  $\times 10^5$  (1, 3, 7, 12). In some cases (1, 5) temperature corrections have been made to 60°F.; in other cases (3, 7, 12, 15) to 25°C.

#### RELATION BETWEEN CONDUCTIVITY AND SALT CONTENT

A number of 1:1 extracts (1 part of soil to 1 part of distilled water) were prepared from soils varying widely in salt content. In addition, samples of irrigation water and of drainage water were obtained from different parts of the Okanagan Valley. Determinations of salt content and electrical conductivity were made on each of these solutions. The salt content was determined by evaporating an aliquot to dryness, and the conductivity was determined with an Industrial Instruments Conductivity Bridge, Model RC-1.<sup>3</sup> The electrical resistance readings thus obtained were corrected to 25°C., and were expressed in terms of mhos  $\times 10^5$ . The figures thus obtained are termed, for the sake of simplicity, "conductivity values."

The data obtained are summarized in table 1 and charted in figure 1. The equation of the curve in figure 1 is  $s = 7.8 c + 0.01535 c^2$ , in which  $s$  = salt content, in parts per million, and  $c$  = conductivity, in mhos  $\times 10^5$  at 25°C.

It is recognized that there are major variations from district to district in the type of salt contained in the soil solution and in the irrigation water. A curve established in any one locality could therefore not be applied in another locality without a preliminary check with a number of samples (2). The curve in figure 1 illustrates, however, that for routine work such a curve may be established and used in any one district for converting electrical conductivity into parts per million of salt content.

<sup>3</sup> The Industrial Instruments Conductivity Bridge, Model RC-1, contains an A.C. bridge with cathode ray visual null indicator (electric eye). It measures the specific resistance of electrolytes from 0.2 to 250,000 ohms. The cell used in this investigation had a cell constant of 2.34, which was found to be satisfactory for the range of resistances encountered. The platinized electrodes were protected by a cylinder of heavy rubber.

## EFFECTS OF SOIL:WATER RATIO ON CONDUCTIVITY

The procedure used in testing the effects of an increasing ratio of water to soil was to mix each soil sample with distilled water in soil:water ratios of 2:1,

TABLE 1  
*Relation between conductivity and salt content*

SOLUTION NUMBER	CONDUCTIVITY VALUE*	SALT CONTENT
		<i>p p m.</i>
52	12	96
53	3	33
54	4	73
55	8	81
56	4	51
57	30	241
58	34	286
59	5	56
60	74	634
61	39	293
62	4	60
63	50	465
64	3	50
65	2	36
66	2	34
67	4	39
68	37	294
69	55	441
70	8	77
71	3	59
72	16	109
73	41	323
74	2	27
75	3	39
80	92	848
81	250	3017
82	377	5128
83	58	509
84	153	1650
85	45	400
86	330	4150
87	109	1200
88	200	2040
89	72	650
90	39	330
91	101	1040
92	47	388

\* Conductivity expressed as mhos  $\times 10^6$ , at 25°C.

1:1, 1:2, 1:4, 1:8, 1:16, and 1:32, let each mixture stand overnight, mix again, let settle for an hour, and take a resistance reading on the supernatant liquid without filtering. With five samples, additional readings were obtained at

ratios of 1:64 and 1:128, as well as at or close to the moisture-holding capacity. For this last, a soil tube somewhat similar to that suggested by Burd and Martin (4) was used, with the moisture forced out the bottom end by a low pressure (10 to 20 pounds) of nitrogen applied at the top. In one series of these tests at the moisture-holding capacity, the tube was filled with dry soil, water was added at the top until it started to drip out the bottom, and the soil was allowed to stand wetted overnight before pressure was applied. In a second series of tests, the same procedure was used, except that the tube was turned upside down while being wetted.

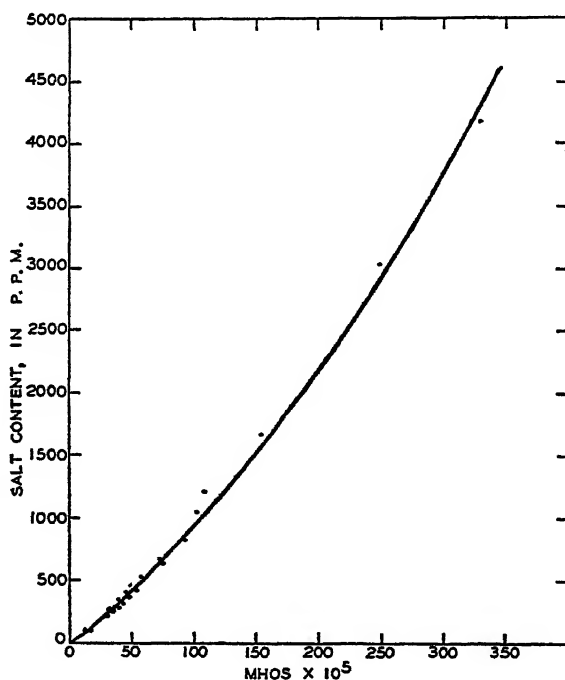


FIG. 1. SALT CONTENT—CONDUCTIVITY CURVE

The equation of this curve is  $s = 7.8c + 0.01535c^2$ , in which  $s$  = salt content in parts per million and  $c$  = conductivity in mhos  $\times 10^5$ , at 25°C.

In these tests at moisture-holding capacity, higher conductivity values were obtained when the tube was wetted right-side up than when it was wetted upside down. This appeared to be due to the transportation of dissolved salts in the advancing water front as the soil was wetted, resulting in a higher accumulation at the bottom of the tube when wetted from the top, and at the top of the tube when wetted from the bottom. The first liquid obtained was always that forced out from the bottom of the tube. The most reliable figure for each soil appeared to be that obtained by averaging the two values obtained by the two methods of wetting, and this, accordingly, was the figure used.

Some of the soil samples used were obtained from orchard fertilizer plots, and some from saline areas. The results obtained are summarized in table 2, and some of them are charted in figure 2. In figure 2, the values for conductivity and for percentage of water are both expressed in terms of their logarithms. On this basis, many of the curves were straight or almost straight between ratios of 1:0.5 and 1:32. With some soils, the conductivity values were lower at 1:0.5 ratio than at 1:1 ratio. In all such cases, these soils contained such high percentages of clay that at the 1:0.5 ratio the unfiltered mixture was very thick

TABLE 2  
*Electrical conductivity as affected by soil:water ratio*

SOIL NUMBER	M.H.C.*	CONDUCTIVITY† AT FOLLOWING SOIL:WATER RATIOS									
		M.H.C.	1:0.5	1:1	1:2	1:4	1:8	1:16	1:32	1:64	1:128
	<i>per cent</i>										
201	22.2	582.0	243.3	125.0	67.7	35.4	21.7	11.8	6.9	4.7	3.8
206	22.9	123.0	54.8	40.0	22.3	17.6	14.8	10.4	9.3	8.3	7.0
211	34.8	642.5	460.8	295.5	193.3	115.6	68.6	40.3	25.1	18.2	13.3
212	38.2	184.8	101.4	70.2	44.8	27.6	19.4	14.2	9.8	7.2	5.6
507	23.5	286.7	132.1	60.6	52.7	26.0	16.8	9.3	5.1	3.5	2.6
49			24.0	18.0	9.5	6.8	4.5	3.9	3.1		
63			56.6	36.5	22.2	13.3	8.9	5.7	4.0		
119			1510.0	1488.0	1290.0	910.0	580.0	351.0	200.0		
121			5380.0	5380.0	3600.0	2340.0	1416.0	816.0	501.0		
122			2130.0	6440.0	4550.0	3540.0	2115.0	1209.0	646.0		
508			64.3	34.5	64.2	35.3	23.5	14.1	10.1		
528			36.6	52.5	32.4	22.6	15.5	11.9	8.9		
K 2			7.9	11.7	6.4	4.3	2.8	2.0	1.4		
K 8			34.0	42.5	26.8	17.8	14.6	11.9	8.9		
K 9			50.0	32.0	21.1	14.4	9.9	8.0	7.0		
K10			18.3	26.9	18.6	10.0	7.1	4.2	3.2		
K18			36.0	27.5	16.4	9.9	7.0	4.9	3.3		
K39			13.1	9.6	6.6	3.6	2.4	1.8	1.3		
K48			38.4	23.9	13.4	8.5	5.0	4.0	3.2		
K49			47.9	25.5	14.6	8.3	6.4	4.1	3.3		
K53			11.7	7.6	4.8	3.0	2.1	1.5	1.2		
S10			9.6	15.6	9.3	6.4	5.0	2.4	1.5		

\* M.H.C. = moisture-holding capacity.

† Conductivity expressed as mhos  $\times 10^5$ , at 25°C.

and pasty. As pointed out by Magistad *et al.* (12), it appears that the direct determination of the resistance on a thick soil paste is not reliable.

The results obtained in this test are in conformity with those reported by other investigators (1, 12, 14), in that the conductivity values decreased rapidly as the ratio of water to soil was increased. This points to the conclusion that if it is desired to compare soil samples on the basis of their electrical conductivities, it is not safe to use a high ratio of water to soil. Furthermore, where standards are being developed for application to soils varying widely in texture,

it may not be safe to use a constant, even though low, ratio (such as 1:1). There is a good deal to be said for the belief (12, 14) that soil solutions should be obtained at or close to the moisture-holding capacity, which of course varies widely with the texture of the soil.

One difficulty with obtaining solutions at the moisture-holding capacity is the length of time involved. Where a large number of routine determinations are being made, some easier method would appear desirable. One possibility is to use a constant multiple of the moisture content at the moisture-holding capacity and to establish standards of comparison on this basis. A convenient ratio appears to be five times the moisture-holding capacity. With as little as

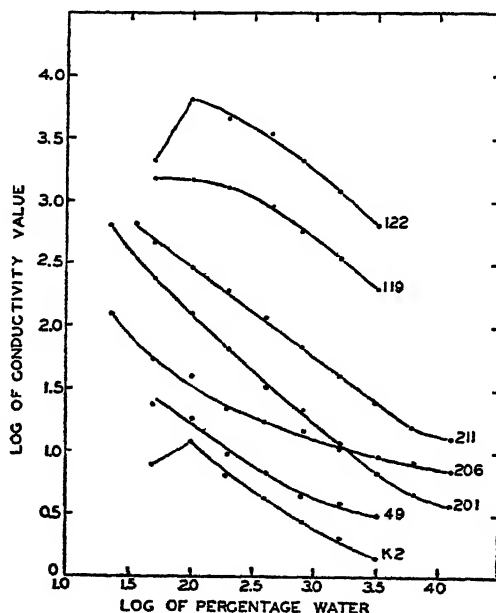


FIG. 2. SOME LOGARITHMIC CURVES OF CONDUCTIVITY VALUES PLOTTED AGAINST PERCENTAGE WATER

The conductivity values are in terms of  $\text{mhos} \times 10^5$ , at  $25^\circ\text{C}$ .

100 gm. of soil, this supplies sufficient filtrate or supernatant liquid for resistance readings. At the same time, it makes allowance for differences between soils in their moisture-holding capacities.

The question arises as to whether the effect of differences in moisture-holding capacity is really worth stressing. To check on this, the conductivity values were determined on 30 soil samples after the solution was obtained by two methods: first, with a 1:1 mixture; and second, with the addition of sufficient water to equal five times the moisture-holding capacity. In both cases, the mixtures were stirred, let stand about 24 hours, again stirred, and let settle for an hour or more. Determinations were then made on the supernatant liquid. The results are summarized in table 3.

Also included in table 3 are the ratios obtained by dividing the conductivity values determined at five times the moisture-holding capacity by those determined at the 1:1 ratio. It will be seen that these ratios varied from as low as 0.78 to as high as 1.47; in other words, the highest ratio was almost twice

TABLE 3  
*Comparison of conductivity values determined at 1:1 soil:water ratio and at five times moisture-holding capacity*

SOIL NUMBER	M.H.C.†	CONDUCTIVITY VALUES*		
		At $5 \times \text{M.H.C.}$	At 1:1	Ratio $\frac{5 \times \text{M.H.C.}}{1:1}$
A 1	13.8	25	22	1.14
A 2	15.6	112	89	1.33
A 3	18.0	26	25	1.04
A 4	15.0.	37	34	1.09
A 5	15.0	26	20	1.30
A 6	15.9	33	26	1.27
A 7	16.0	25	23	1.09
A 8	19.2	22	20	1.10
A 9	16.2	58	49	1.18
A10	16.2	29	28	1.04
A11	14.0	16	13	1.23
A12	21.0	31	36	0.86
A13	13.6	25	20	1.25
A14	17.4	48	42	1.14
A15	17.4	45	35	1.28
A16	22.0	52	60	0.87
A17	23.4	43	51	0.84
A18	20.4	58	59	0.98
A19	15.2	40	31	1.29
A20	16.0	39	35	1.11
A21	12.4	31	21	1.47
A22	12.6	330	275	1.20
A23	12.6	47	35	1.34
A24	18.0	38	35	1.09
A25	16.4	294	265	1.11
A26	22.0	175	174	1.01
A27	15.6	60	51	1.18
A28	28.8	206	264	0.78
A29	23.4	164	167	0.98
A30	15.0	293	248	1.18

\* Conductivity values =  $\text{mhos} \times 10^5$ , at  $25^\circ\text{C}$ .

† M.H.C. = moisture-holding capacity.

as high as the lowest. This effect of difference in method of obtaining the solution appears, then, to be well worth serious consideration. The table shows, further, that the highest ratios occurred on those soils with the low moisture-holding capacities, and the lowest ratios on those soils with the high moisture-holding capacities. It was found that the correlation between the

moisture-holding capacity and the conductivity ratio was  $-0.85$ , a "highly significant" value (odds greater than 99:1). This means that the conductivity values determined at the 1:1 ratio were too low with sandy soils and too high with clay soils, in comparison with the values determined at five times the moisture-holding capacity.

A number of laboratory methods of determining the moisture-holding capacity have been suggested in previous papers by the author (16, 17). The more promising of the methods tried involved the use of mechanical analyses or of settling volume determinations. A method now used in this laboratory for rough conductivity determinations at five times the moisture-holding capacity is as follows:

Place 100 gm. of air-dry soil in a tall jar or beaker 2 to 2½ inches in diameter. Measure out 100 ml. of water, and with as much of it as necessary wet the soil to the "stirring point."

TABLE 4  
*Electrical conductivity as affected by filtering*

SOIL NUMBER	CONDUCTIVITY VALUES*	
	Before filtering	After filtering
US2	27	28
US8	30	34
US9	21	24
US10	18	23
US11	18	20
US12	37	40
K9 (2:1)	50	52
K9 (1:1)	32	35
K9 (1:1)	34	35
K9 (1:2)	21	23
K9 (1:4)	15	17
K9 (1:8)	10	12
K9 (1:16)	8	10

\* Conductivity values in mhos  $\times 10^5$ , at 25°C.

To determine this point, add the water in aliquots, stirring with a steel stirring rod after each addition. Place a folded towel on the bench and tamp the jar on it lightly five times after each stirring. When the surface of the mixture is smooth and level after the tamping, the "stirring point" has been reached. This is somewhat similar to Doughty's "paste point" (6). Determine the amount of water used, and add twice as much more, so that the moisture content is at three times the stirring point. This is equal to approximately five times the moisture-holding capacity as determined under field conditions. The mixture is then used for determination of electrical conductivity.

This method does not work well with coarse sands or peats.

#### EFFECTS OF FILTERING

To test the effects of filtering, 1:1 ratio mixtures of six soil samples were stirred, let stand 24 hours, stirred again, and let stand approximately one hour.

Resistance readings were made on the supernatant liquid. In each case, the aliquot used was returned to the mixture, which was then filtered through a No. 5 Whatman paper, and a reading was made on the filtrate. Similar tests were made on a seventh soil at soil:water ratios varying from 2:1 to 1:16. The results are presented in table 4.

Filtering induced a small increase in the conductivity values in every case. The reason for this has not been ascertained. Where accuracy is necessary, it appears from this that the mixtures should be filtered. For routine work, however, the increase in accuracy does not appear to be worth the additional labor involved. The practice adopted at this laboratory has been to set up soil conductivity standards on the basis of the supernatant solutions, and to make routine determinations for farmers by this procedure.

#### EFFECTS OF LENGTH OF TIME AFTER MIXING

Five soil samples were mixed with water in 2:1 soil:water ratios. Each mixture was stirred, let stand 1 hour, stirred, and allowed to settle for a few

TABLE 5

*Electrical conductivity as affected by time after mixing*

SOIL NUMBER	TEXTURAL TYPE	CONDUCTIVITY* VALUES AT INTERVALS AFTER MIXING					
		1 hour	2 hours	4 hours	1 day	2 days	4 days
201	Subsoil sand	9.8	10.1	10.2	10.3	10.3	10.7
203	Surface clay	14.4	16.5	17.4	21.6	21.5	19.9
205	Gravelly subsoil	13.4	14.3	14.8	14.8	14.8	14.6
208	Sandy loam	20.0	21.0	22.0	23.0	23.0	25.0
507	Sandy loam	7.2	7.8	8.0	7.9	7.3	7.4

\* Conductivity values in mhos  $\times 10^5$ , at 25°C.

minutes. A resistance reading was then taken on the supernatant liquid. The aliquot used was returned to the mixture, which was again stirred. Readings were taken in a similar manner at 2 hours, 4 hours, 1 day, 2 days, and 4 days after the first mixing. The results, presented in table 5, show that the conductivity tended to increase up to 24 hours, after which it rose a little with two samples and fell a little with the other three samples. These results indicate that a period of 24 hours is reasonably satisfactory. This is in conformity with the procedures now being used by a number of investigators (1, 14).

#### PROCEDURE ADOPTED

The procedure now used in this laboratory is as follows:

1. Wet 100 gm. of soil to five times the moisture-holding capacity. For routine determinations, this is done by wetting to three times the stirring point.
2. Stir thoroughly, let stand 20 to 24 hours, stir, let settle 1 hour, and determine electrical resistance on the supernatant liquid.
3. Express results in terms of mhos  $\times 10^5$ , at 25°C. No attempt is made to convert results into parts per million of salt content.



This procedure is being used in studies of the effect of soil salinity on plant growth under field conditions in the southern interior of British Columbia.

#### SUMMARY

A study was made of the use of electrical resistance for determining the salt content of soil solutions.

The electrical conductivity ( $\text{mhos} \times 10^6$ ) and the actual salt content were determined on a number of solutions varying widely in salt content. A relationship close enough to warrant the use of the resistance meter for routine work was found to exist between the two measurements.

In studies of the effects of soil dilution, extracts were obtained at the moisture-holding capacity and at soil:water ratios varying from 1:0.5 to 1:128. The electrical conductivity showed a progressive decrease with dilution. It is suggested that determinations should be made either at the moisture-holding capacity or at some constant multiple of the moisture-holding capacity.

Resistance determinations made directly on a thick soil paste were found to be unreliable. Filtering a supernatant solution raised its conductivity value slightly. When a soil-water mixture was allowed to stand, the conductivity values increased for about 24 hours, then showed little change.

The procedure adopted involved wetting the soil to about five times the moisture-holding capacity, stirring, letting stand 20 to 24 hours, stirring again, letting settle 1 hour, and taking an electrical resistance reading on the supernatant liquid without filtering. The results are expressed in terms of  $\text{mhos} \times 10^6$ , at 25°C.

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# SYMBIOTIC STUDIES WITH ISOLATES FROM NODULES OF SPECIES OF ASTRAGALUS

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Reports continue to appear in the literature concerning the specificity of the relations existing between certain leguminous plants and their associated organisms. Such reports keep alive the idea that a boundary can be drawn around a group of plants within which a specific organism such as *Rhizobium trifolii* will cause nodules to develop only on the plants within the boundary. They appear despite the fact that other data are interpreted as indicating that no specific organism has been found for a group of plants or for a single plant. The concept probably still survives because of one or more of several conditions. It may exist because of the unavailability of the published data, the limited scope of the tests, the particular methods and technique employed, or other conditions that modify the results.

Perhaps the first report dealing with species of *Astragalus* and their associated organisms was that of Bushnell and Sarles (2). These investigators worked with four species of the genus. Their findings, they concluded, lend weight to the probability that *Astragalus* species comprise their own select cross-inoculation group. The isolates from nodules of these four species were much alike, the organisms all being monotrichous. They did not effect nodules on species of other legumes, nor did isolates from other legumes cause nodules to develop on any one of the four species from which these isolates came. Studies of the morphology and of the cultural characteristics of isolates from species of *Astragalus* made by Aso and Ohkawara (1) and by Itano and Matsuura (4) indicated also that the bacteria were of a uniform type.

Data published by Wilson (6) were concerned with the relationships of 32 strains of the legume bacteria with nine species of this genus; none of the isolates came from plants of species of *Astragalus*. The author found among other things that excellent nodules developed on seedlings of *Astragalus rubyi* Green and Morris after exposure to isolates from *Caragana frutescens* DC., *Crotalaria spectabiles* Roth., *Dalea alopecuroides* Willd., and *Desmodium canadense* (L.) DC. and that good or fair nodulation appeared on seedlings of *A. Cicer* L., after exposure to an isolate from *Cassia fasciculata* L., *Crotalaria spectabilis* Roth., *Dalea alopecuroides* Willd., *Lens esculenta* L., *Lespedeza striata* Hook & Arn., *Lupinus perennis* L., *Oxytropis Lambertii* Pursh., *Swainsona coronillaefolia* Salisb., *Trifolium pratense* L., *Vicia villosa* Roth., and to an isolate from *Wisteria chinensis* DC. From the data it was evident, further, that the nine species of *Astragalus* employed could be distributed among eight of the invalid cross-inoculation groups.

Chen and Shu (3) have presented their studies of work performed during 3 years relating to the root-nodule bacteria of *Astragalus sinicus* L. They contend

that the root-nodule bacteria from this plant do not effect nodules on other genera of leguminous plants, nor do bacteria isolated from other sources, except one, effect nodules on plants of *Astragalus*. Hence they conclude that *Astragalus* and its root-nodule bacteria must be considered as a select cross-inoculation group.

In a study of the nodulating performance of three species of legumes in which 21 isolates from nodules of 21 species of *Astragalus* were employed, Wilson (7) observed that each of these effected nodules on *Amorpha fruticosa* DC., 15 on *Crotalaria sagittalis* L., and all 21 on *Wisteria chinensis* DC. It is evident from these data, therefore, that the bacteria from certain genera, not including the *Astragalus*, will effect nodules on certain species of *Astragalus* and that the bacteria from 21 species of *Astragalus* will symbiose with plants that are not in the genus *Astragalus*. By studying the symbiotic performance of isolates from soybean, Wilson (8) found that three of twelve isolates obtained from nodules of this species symbiosed with plantlets of *Astragalus Nuttalianus* DC. It would appear, therefore, that the species of this genus do not comprise one select cross-inoculation group. Further evidence that such is the case is presented in this paper. Many of the data reported previously (6, 7, 8) were obtained by exposing plantlets of species of *Astragalus* to isolates not from species of *Astragalus*, whereas the data reported here were obtained principally by employing isolates from species of *Astragalus* to determine their nodulating abilities on species of *Astragalus* and on other legumes.

#### METHODS

To obtain evidence as to whether the species of *Astragalus* comprise one select cross-inoculation group, slight modifications were made in the laboratory and greenhouse procedures previously described by Wilson (6), although the methods are essentially the same. The modifications consisted in wetting the soil in the glass containers with water containing 0.05 per cent of sucrose and 0.05 per cent of monopotassium phosphate and sterilizing the entire equipment in steam either at 15 to 20 pounds' pressure for 6 hours or at 50 to 60 pounds for 3 hours. The quantity of sandy soil in any container never exceeded 2000 gm. and the depth was never less than 1.5 inches in any container. After the seeds were etched in concentrated sulfuric acid, washed, and treated with a filtered solution of calcium hypochlorite they were dropped on the surface of the soil in the containers with some of the sterilizing agent adhering to them. In most cases the seeds were covered by dribbling sterilized sandy soil over them in the containers. This soil was sterilized as above in test tubes. Controls were always provided, and all containers were kept in a greenhouse for 30 to 50 days.

The isolates employed were obtained from nodules of species of *Astragalus* and certain other plants and symbiosed with plantlets of the species from which they were obtained. The plants from which the data came were grown at various periods during the year. Some attempts in summertime were largely failures owing to excessive heat or other environmental conditions. As a result,

supplementary and replicatory tests were made. In some instances the tests were repeated six times, in others only twice. Any procedure not mentioned here that might be helpful in interpreting the data is described in connection with the particular test where it is used. The seeds of the various species used were obtained from experimental stations in the United States or from the Soil Conservation Service of the U. S. Department of Agriculture and were considered to be correctly identified.

TABLE 1

*Symbiotic relations of species of Astragalus with isolates from 21 species of this genus*

PLANTS FROM WHICH ISOLATES CAME	NODULATION* OF PLANTS EXPOSED TO ISOLATE																				
	<i>A. chinensis</i>	<i>A. Cicer</i>	<i>A. colteri</i>	<i>A. crassicaarpus</i>	<i>A. Echinus</i>	<i>A. falcatus</i> Lam	<i>A. lonchocarpus</i>	<i>A. Menziesii</i>	<i>A. mortoni</i>	<i>A. Nuttallianus</i>	<i>A. onobrychis</i>	<i>A. pectinatus</i>	<i>A. pomonensis</i>	<i>A. rubyi</i>	<i>A. semibilocularis</i>	<i>A. sinicus</i>	<i>A. succulentus</i>	<i>A. utahensis</i>	<i>A. verus</i>	<i>A. wootoni</i>	
<i>A. adpressus</i> Labill .....																					
<i>A. bisulcatus</i> A. Gray .....	+					+			+	+										+	
<i>A. branchocarpus</i> Bieb .....	+									+											
<i>A. chinensis</i> L. ....	+					+			+	+											
<i>A. Cicer</i> L. ....		+			+				+	+											
<i>A. colteri</i> Benth. ....			+						+	+											
<i>A. crassicaarpus</i> Fras. ....				+					+	+											
<i>A. Echinus</i> G. A. May .....					+	+		+	+	+	+		+				+				
<i>A. membranaceus</i> Moench. ....									+	+											
<i>A. Menziesii</i> A. Gray .....		+				+		+	+	+			+								
<i>A. mortoni</i> Nutt .....	+						+		+	+				+	+	+			+	+	
<i>A. Nuttallianus</i> DC. ....		+				+			+	+											
<i>A. onobrychis</i> Polle .....									+	+	+						+			+	
<i>A. pectinatus</i> Boiss .....		+							+	+		+					+				
<i>A. rubyi</i> Green & Morris .....	+					+		+	+	+				+	+	+	+			+	
<i>A. semibilocularis</i> DC .....	+			+					+	+		+			+		+				
<i>A. sinicus</i> Thumb .....	+	+						+	+	+	+					+	+			+	
<i>A. succulentus</i> Richards .....									+	+	+			+	+		+			+	
<i>A. utahensis</i> Torr. and Gray .....	+					+		+	+	+	+			+	+			+			
<i>A. verus</i> Georgi .....		+			+	+		+	+	+	+		+	+	+			+	+	+	
<i>A. wootoni</i> Sheldon .....	+				+	+		+	+	+		+		+	+			+	+	+	

\* The plus (+) indicates that nodules were present.

## RESULTS OF STUDIES

The methods employed made it possible to protect the plantlets from contamination with legume bacteria during growth, thus adding confidence to the findings. Although the conditions under which the plants grew may not have been conducive to the best growth they did provide certain data from which to draw conclusions.

### *Symbiotic relations of species of Astragalus with isolates from the same species*

Some of the evidence obtained from this study concerning the relations existing between the plants of various species of the *Astragalus* and the bacteria isolated from nodules of 21 species of this genus is presented in table 1. It is apparent



found that plantlets of each genus failed to symbiose with certain isolates from the nodules of other species, tests were made to ascertain the symbiotic relations between certain species of legumes and isolates of the bacteria from nodules of species of *Astragalus*. The data obtained from such a test are given in table 2. In this test the same 21 isolates that are shown in table 1 were employed again. Twenty-three species (27 if those listed in table 3 are included) of legumes were exposed to one or more of the 21 isolates. The data are sufficiently extensive to permit the statement that no boundary can be placed around the bacteria that effect nodules on various species of *Astragalus* which will separate them from organisms that will cause nodules to develop on many species of plants

TABLE 3

*Some relations of isolates from species of Astragalus with species of Trifolium as revealed by nodulation*

PLANTS FROM WHICH ISOLATES CAME	NODULATION* OF PLANTS EXPOSED TO ISOLATE			
	<i>T. arvense</i>	<i>T. hybridum</i>	<i>T. pratense</i>	<i>T. repens</i>
<i>A. adpressus</i> .....	+S	+F	+K	+K
<i>A. bisulcatus</i> .....	+K	+K	+S	+K
<i>A. Cicer</i> .....				+P
<i>A. colteri</i> .....	+S			
<i>A. crassicaupus</i> .....	+K	+K	+K	+S
<i>A. Echinus</i> .....			+K	
<i>A. Menziesii</i> .....	+P			
<i>A. semibilocularis</i> .....	+K		+P	
<i>A. succulentus</i> .....	+K	+K	+S	+SK
<i>A. utahensis</i> .....				+
<i>A. verus</i> .....			+K	
<i>A. wootoni</i> .....			+PA	+F

\* Type of nodulation

A = Atypical

F = Fair—15-25 per cent of plants bear nodules

K = Satisfactory

P = Poor, 1 or 2 nodules on 25 or more plants, sometimes none

S = Excellent.

not included in the genus *Astragalus*. In fact each of the 21 isolates effected nodules on *Wisteria frutescens* and all but one did the same thing on *Amorpha fruticosa*. The isolate from *Astragalus sinicus* caused nodules to develop on 14 of these species.

In order to supplement these data, plantlets of *Astragalus Nuttalianus* were exposed to isolates from a wide range of species. Certain isolates did not effect nodules on plantlets of this species and are not recorded here, but those that did came from the following plants:

*Albizia julibrissin* Durazz., *Amorpha canescens* (Nutt) Pursh., *A. fruticosa* DC., *Cara-gana frutescens* DC., *Cassia fasciculata* Michx. *Cicer arietinum* L., *Chianikus breviolata*, *Crotalaria anagyroides* HBK., *C. falcata* Bahl., *C. intermedia* Kotschy., *C. maxillaris*



Klotzsch., *C. mundyi* Baker, *C. spectabilis* Roth., *Dalea alopecuroides* Willd. (8 isolates), *Dalea aurea* Nutt., *Dorycnium herbaceum* Vill., *Galactia volubilis* (L.) Britton, *Glycine max* (L.) Merr. (3 isolates), *Glycyrrhiza lepidota* Pursh., *Goodia medicaginea* F. Muell., *Lathyrus maritimus* Bigel., *L. pratense* L., *Lebeckia simsiana* Eck. and Zeyh., *Lens esculenta* Moench. *Lespedeza striata* Hook and Arn., *Leucaena glauca* Benth., *Lotus corniculatus* L., *Lysiloma thornberi*, *Medicago sativa* L. (2 isolates), *Neptunia plena* Lindl., *Ononis fruticosa* L., *O. Natrix* L., *Oxytropis Lambertii* Pursh., *Parryella filifolio* T. & G., *Petalostemon purpurea* (Vent.) Rydb., *Phaseolus coccineus* L., *Phaseolus vulgaris* L., *Schrankia uncinata* Willd., *Sesbania exultata* Muhl., *Sutherlandia frutescens* R. Br., *Swainsona coronillaefolia* Salisb., *Trifolium agrarium* L., *T. ambiguum* Bieh., *T. fragiferum* L., *T. pratense* L. (3 isolates),

TABLE 4

Variability of isolates from species of *astragalus* as ascertained by growth in a liquid medium containing nitrate\*

PLANT FROM WHICH ISOLATE CAME	CONCENTRATION TO INHIBIT TURBIDITY BY GROWTH	CONCENTRATION GIVING BEST GROWTH AS REVEALED BY TURBIDITY	GREATEST CONCENTRATION GIVING NITRITE	NO NITRATE IN CONCENTRATION BELOW	CONCENTRATION GIVING MOST NITRITE
<i>A. adpressus</i> .....	50,000	500	50,000	5,000	50,000
<i>A. bisulcatus</i> .....	5,000	500	500	500	500
<i>A. branchocarpus</i> .....	25,000	500	25,000	2,500	25,000
<i>A. chinensis</i> .....	25,000	500	10,000	5,000	5,000
<i>A. Cicer</i> .....	50	500	5,000	5,000	5,000
<i>A. colteri</i> .....	50,000	5,000	25,000	25,000	25,000
<i>A. crassicaarpus</i> .....		500	5,000	50	50
<i>A. Echinus</i> .....	25,000	50	10,000	500	5,000
<i>A. membranaceus</i> .....	50,000	5,000	10,000	500	10,000
<i>A. Menziesii</i> .....	10,000	5,000	500	50	500
<i>A. mortoni</i> .....	50,000	5,000	10,000	5,000	10,000
<i>A. Nuttalianus</i> .....	25,000	500	5,000	5,000	5,000
<i>A. onobrychis</i> .....	25,000	500	5,000	5,000	5,000
<i>A. pectinatus</i> .....	50,000	25,000	50,000	25,000	50,000
<i>A. rubyi</i> .....	>50,000	10,000	10,000	5,000	5,000
<i>A. semibilocularis</i> .....	50,000	5,000	5,000	5,000	25,000
<i>A. succulentus</i> .....	5,000	50	5,000	5,000	5,000
<i>A. utahensis</i> .....	50,000	10,000	50,000	5,000	50,000
<i>A. verus</i> .....	25,000	5,000	10,000	5,000	10,000
<i>A. wootoni</i> .....	25,000	50	5,000	500	5,000

\* Incubated at 24-26°C. for 10 days. Concentrations of NaNO<sub>3</sub> employed—0, 50, 500, 5000, 10,000, 25,000, 50,000 p.p.m.

*T. repens* L., *Vicia faba* L., *V. villosa* Roth., *Vigna sinensis* Endl., *Virgilia capensis* Lam., *Wisteria chinensis* DC., *W. floribunda alba* DC., *W. frutescens* (L.) Poir. (3 isolates).

#### *Some relations of isolates from Astragalus with species of Trifolium*

Additional supporting data were obtained concerning the promiscuous nature of the strains from *Astragalus*. Such information came by exposing plantlets of four species of *Trifolium* to the 21 isolates and by subsequently examining the roots for nodules. The results are presented in table 3. Only those isolates that effected nodules on one or more species of *Trifolium* are listed. It is plain

from the data that 11 of the 21 isolates were closely related to, if not identical with, those strains that might be isolated from nodules of species of *Trifolium*, for four effected nodules on all four species of *Trifolium*, whereas six were not so closely related, each effecting nodules on one species only.

*Variability of isolates from species of Astragalus as ascertained by growth in a medium containing nitrate*

Since the present findings indicate that the isolates from the various species of *Astragalus* are dissimilar, corroborative evidence was sought concerning this variability by growing some of the isolates in a nutritive solution, to portions of which sodium nitrate and 2 per cent of sucrose were added. The concentrations of the salt were 0, 50, 500, 5,000, 10,000, 25,000, and 50,000 p.p.m. This medium was sterilized in test tubes and kept at 24–26°C. for 10 days after having been inoculated with the desired isolates. The measure of variation was the ability of the isolates to grow in the medium as revealed by turbidity and to reduce the nitrate to nitrite as determined by means of the Greiss reagents. A summary of the findings is given in table 4.

If the differences in growth of the organisms from the various species of *Astragalus* in the medium containing nitrate as ascertained by turbidity represent variations among isolates, it is evident that the organisms differ considerably. Some of them grew luxuriantly in the medium containing as much as 10,000 p.p.m. of  $\text{NaNO}_3$ , whereas others grew best where only 500 p.p.m. was present.

Also some isolates appeared to be unable to effect a reduction of nitrate unless the salt was present in larger quantities than 10,000 p.p.m., whereas others brought about the reduction where only 50 p.p.m. were present. Further, some of the isolates reduced more nitrate when the concentration was high; others when the concentration was low. As an illustration the isolate from *A. adpressus* reduced the greatest amount of nitrate when the concentration of the salt was 50,000 p.p.m., whereas the isolate from *A. Menziesii* effected the greatest reduction when 500 p.p.m. was present.

#### DISCUSSION

The data presented substantiate and extend those published previously to the effect that the species of *Astragalus* and their associated organisms do not comprise one select cross-inoculation group as suggested by the data of previous workers. This statement can be made because no isolate from any species of *Astragalus* was found that would effect nodules on each species of *Astragalus* employed in this work and because plantlets of *A. Nuttallianus* bore nodules after exposure to 67 isolates obtained from nodules of 53 species representing 36 genera of the legumes. In addition, the 21 isolates from the 21 species of *Astragalus* effected nodules on one or on more than one of 23 species of legumes not belonging to the genus *Astragalus*. In fact, each isolate from the 21 species effected nodules on plantlets of *Wisteria frutescens* (L.) Poir. and also all isolates, except one, did likewise on plantlets of *Amorpha fruticosa* L.

If the ability of an isolate to cause nodules to develop on a plant can be considered as a criterion of the cross-inoculation group to which the plant belongs, then it is evident that each species of *Astragalus* could be assigned to two or more groups of the proposed cross-inoculation groups for classifying these organisms and their associated plants. *Astragalus adpressus* could be assigned to three groups and *A. Echinus*, *A. Nuttalianus*, and *A. wootoni* each could be assigned to five groups. Likewise, if the species of *Astragalus* and their associated organisms comprise one select cross-inoculation group, then certain proposed groups should be abandoned. These groups would be Alfalfa, Amorpha, Bean, Clover, Cowpea, Dalea, Lotus, and Pea, because isolates from nodules of species of *Astragalus* have effected nodules on plantlets of species that have been assigned to these eight groups.

The fact that the isolates from species of *Astragalus* effected nodules on plantlets of many genera of the legumes indicates that these isolates could be isolated at one time or another from such plants. The fact that these plants may be representatives of several of the proposed cross-inoculation groups, as shown by the data in this paper as well as by data published elsewhere, emphasizes again the difficulty of assigning names to organisms that are supposed to associate only with a certain prescribed group of plants. The finding that certain isolates effected nodules on the plantlets of all four species of *Trifolium* whereas others effected nodules only on one of the four is of considerable additional significance. It shows variation in isolates and places the emphasis on the particular strain rather than on a group of plants that might bear nodules after exposure to the isolate. Since the name *Rhizobium trifolii* has been given to the one organism that may effect nodules on species of *Trifolium*, the question may be asked: What shall be the name of the organism that does not effect nodules on plants of all species of this genus but only on plants of one or two species? Many other strains exist also that will effect nodules on one or on several species which differ in their symbiotic relations from those given here.

There is no more reason for thinking that the species of *Astragalus* and their associated organisms comprise one select cross-inoculation group than there is to think that the species of such genera as Lotus, Medicago, Phaseolus, Pisum, or Vigna and their associated organisms each comprise one select group. In such cases the relations existing between the various species of a genus and their associated organisms are too heterogenous to be classified by those characters that constitute a genus. Such heterogeneity apparently exists even in seed of a single plant, for Wilson (9) pointed out that plantlets grown from seed of one plant may symbiose with a certain strain of the organism whereas plantlets grown from seed of another plant of the same species may not symbiose with the same strain. Paralleling such data are the findings of Nuttman (5) concerning genetical factors in the symbiosis of clover and nodule bacteria. He found a red clover plant that bore no nodules after exposure to a certain culture of the root-nodule bacteria whereas other plantlets of this same species did bear nodules after exposure to the same culture. When this unique plant was casually pollinated, the breeding behavior suggested that lack of nodules is recessive and that a number of genes are concerned.

The apparent inability of strains to effect a reduction of nitrate unless the nitrate was present within a certain prescribed amount provides an explanation for some of the diverse findings that have been reported in the literature concerning the ability or lack of ability of *Rhizobium* to reduce nitrate to nitrite. The isolate from *Astragalus colteri* effected a reduction at a concentration of 2.5 per cent of  $\text{NaNO}_3$ , but it did not do so where 0.5 per cent was present. Likewise, the isolate from *A. Menziesii* effected no reduction at a concentration above 0.05 per cent, but it did effect a reduction at this and at a lower concentration. Other comparisons are given in table 4. Such data coincide with those already published (6). It may be suggested, therefore, that an isolate from any legume may effect a reduction of nitrate to nitrite if the proper concentration and environmental conditions are provided.

#### SUMMARY AND CONCLUSION

This study was designed to show the relations existing between species of *Astragalus* and the root-nodule bacteria isolated from them. Plantlets were exposed to the isolates, and the presence of nodules was the criterion of such a relation. It was observed that there is no specific organism for plants of this genus, for isolates from nodules of species of *Astragalus* effected nodules on plantlets of other genera some of which are representatives of several of the invalid cross-inoculation groups. The findings are discussed in relation to the findings of other workers, to the classification of the bacteria, and to the cross-inoculation groupings. It is concluded that the *Astragalus* and their associated organisms do not comprise a select cross-inoculation group and that the data support the reasons previously given for abandoning such a scheme of classification.

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# THE NUTRITIVE VALUE OF PLANTS GROWN WITH AND WITHOUT SOIL

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The view has been expressed (3, 4) that common foods now generally produced with the aid of artificial inorganic fertilizers are inferior in nutritional quality to those produced, as in former days, in soils fertilized solely with organic manures, or so-called humus. Extensive clinical investigations on adults and infants supplied with vegetables grown in differentially fertilized soils have been reported from Germany (7, 8).

Since all agricultural soils contain varying amounts of organic matter if only from root residues of previous crops, this study was undertaken to appraise the effects of organic matter on the dietetic quality of plants, by feeding to guinea pigs, as a sole source of food, plants grown without soil in an inorganic water culture medium. A parallel group of animals received plants grown under similar conditions in a soil with a history of organic manuring.

The purpose of these experiments was to search not for any one specific nutrient which may be at variance in the plants grown by the two methods, but rather to use the growth curve of the animals supplied with plants, grown in the usual way in soil, as a yardstick to measure the general dietetic adequacy in animal nutrition of plants grown without organic matter in a synthetic inorganic medium. Astoria bent grass was grown by both methods and fed to guinea pigs. The use of one species of plants grown by the two methods as the *sole* food in an animal feeding experiment has afforded a test for the adequacy of all nutritional factors including those which may be at present unknown. The data presented also bear on the question, sometimes raised, of possible toxicity to animals of plants grown without soil in an artificial nutrient medium.

## METHODS

### *The growing of plants*

The previously described (2, 5) large-scale water-culture methods have been used for growing plants without soil. Black iron tanks, coated with black asphaltum paint, 120 by 30 by 8 inches deep and holding approximately 460 liters of nutrient solution were used as containers for growing plants. Astoria bent grass seed was spread between two layers of moist cheesecloth resting over the tank on especially designed covers. The covers consisted of wooden frames covered with burlap sacking dipped in black asphaltum paint. When the seed sprouted, the upper layer of cheesecloth was removed and the roots were allowed

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to penetrate, through the lower layer of cheesecloth and the underlying burlap sacking, into the nutrient solution.

The nutrient solution made with distilled water was of the following composition:  $\text{KNO}_3$ , 0.010 *M*;  $\text{Ca}(\text{NO}_3)_2$ , 0.003 *M*;  $\text{MgSO}_4$ , 0.002 *M*;  $\text{NH}_4\text{H}_2\text{PO}_4$ , 0.002 *M*. A supplementary solution (1) designated *A5* furnished 0.5 p.p.m. each of boron and manganese, 0.05 p.p.m. of zinc, 0.02 p.p.m. of copper, and 0.01 p.p.m. of molybdenum. Iron was added once a week, or as the plants became large, twice weekly at the rate of  $\frac{2}{3}$  cc. of 0.5 per cent iron tartarate solution to a liter of nutrient solution. When the grass was started a one-fourth strength of the nutrient solution was used. The solution was analyzed from time to time, and the inorganic nutrients were replenished as used. Forced aeration was given each tank by means of two porous carbon tubes extending through the length of the tank (2).

The soil plots<sup>2</sup> on which Astoria bent grass was grown constituted a part of an experiment conducted for other purposes by the Division of Agronomy and consisted of six plots of fertile garden soil each occupying an area of 60 square feet. The beds were 4 years old at the time of the experiment. Their fertilization history was as follows. When the soil was first prepared for planting in the fall, each plot was fertilized with 75 pounds of sheep manure and 25 pounds of alfalfa meal. The following spring each plot received 30 pounds of barnyard manure supplemented with  $\frac{1}{4}$  pound each of commercial ammonium sulfate and calcium nitrate. This treatment was repeated in the fall and again in the spring of the following year. Thereafter each plot received alternately every 4 weeks  $\frac{3}{4}$  pound ammonium phosphate or  $\frac{3}{4}$  pound calcium nitrate. For insecticidal purposes lead arsenate at the rate of  $\frac{3}{4}$  pound per plot was added twice, the second application preceding the present experiment by 3 years.

The grass was clipped twice a week, and the clippings were fed to animals directly or were kept for several days in a refrigerator before being fed. The soil and nutrient solution cultures were both kept outdoors.

#### *Feeding experiments*

A preliminary trial conducted with three species of grasses grown in synthetic water-culture media established the palatability to guinea pigs of grass grown without soil by the water-culture method. The three species of grasses were furnished as supplements to a basal diet. In the main experiment ten guinea pigs were put on an exclusive grass diet at the age of between 4 and 6 weeks. For the first 3 weeks after birth their nursing was supplemented with mother's diet consisting of whole milk powder, 33 per cent; ground whole wheat, 51 per cent; wheat germ, 15 per cent;  $\text{NaCl}$ , 1 per cent; supplemented with adequate vitamin A and D from a fish oil concentrate and twice weekly with lettuce; during the remainder of the preliminary period the animals were given Standard Rabbit Pellets (Globe A1) supplemented with wheat germ, vitamin A and D from fish oil, and twice a week with lettuce.

<sup>2</sup> We wish to thank B. A. Madson and T. P. Moody for making available to us the grass clippings from the soil plots.

## RESULTS

The animals were kept on the exclusive grass diet for 12 weeks. Initially they were each given 100 gm. of grass daily. Later, clippings were supplied *ad libitum*; each animal often ate more than 300 gm. daily.

Of the six animals originally included in the group given the clippings from the soil-grown grass, two died in the third week, and of the four guinea pigs receiving the grass clippings from the nutrient solution, one died in the sixth week of the experiment. The comparison was confined then to four guinea pigs receiving the soil-grown grass (two females and one male litter-mates plus one female from another litter) and to three guinea pigs subsisting on the solution-grown grass (two males from the two litters represented in the former group and another female). The growth data are presented in figure 1.

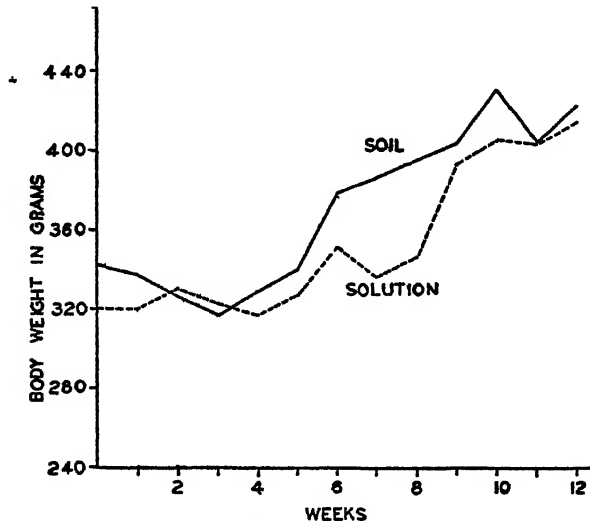


FIG. 1. COMPOSITE GROWTH CURVES OF GUINEA PIGS ON A SOLE DIET OF ASTORIA BENT GRASS GROWN IN SOIL OR NUTRIENT SOLUTION

The animals in both groups showed good growth in length, excellent skeletal and muscular development, good condition of fur, clear eyes, and all the other indications of nutritional well-being. Their outstanding characteristic was the scarcity of fat deposits, which was undoubtedly related to the bulkiness and low caloric value of the diet. It is possible that, particularly toward the end of the experiment, as the animals grew larger the exclusive grass diet, although adequate for growth and maintenance of vigor, was incapable of supplying the optimum caloric requirement.

As indicated by the composite graph in figure 1, the growth data offer no support for a view favoring the nutritional quality of grass produced in soil over that produced in an artificial inorganic medium without soil. Such fluctuations in the growth as were observed are probably within the limits of variability among the animals.



## DISCUSSION

The considerable amounts of grass required for the maintenance of one guinea pig made it impossible, even with the large-scale installation used, to include more than a relatively few animals in the feeding tests. The paucity of the animal population, however, is somewhat offset by the rigidity of the nutritional test, that is, using the grass as the sole source of food. The principal conclusion of this study, that organic matter has no significant function in determining the dietetic quality of plant products is in harmony with the general concept that green autotrophic plants are capable of synthesizing all their organic constituents from the products of photosynthesis, provided they are supplied with all the essential inorganic nutrients (minerals) and are grown under favorable environmental conditions (6). Plants depend on soils not for organic constituents but for water, oxygen, and minerals, which as shown by numerous investigations can be supplied by synthetic inorganic culture solutions. The importance of organic matter in soils lies not in its supply of organic substances for plant growth but rather in its relation to soil management practices, the consideration of which exceeds the scope of this paper.

Mention should also be made about the possible effects on plant nutrition of organic synthesis by microflora. Little can be said about the subject except to note that microorganisms were not excluded by the water-culture technique as used here. Neither would they be excluded from a soil whether receiving inorganic fertilizers or organic manures.

The results of the feeding experiments gave no indication of any toxicity in the grass grown by the water-culture method.

## SUMMARY

The effect of soil organic matter or humus on the nutritional value of plants was studied by feeding to guinea pigs grass grown in a fertile soil with a history of organic manure fertilization and in a large-scale artificial water-culture medium free of humus.

When clippings of Astoria bent grass grown in the two respective media were given as the *exclusive diet* to the groups of guinea pigs for 12 weeks, the animals in both groups made comparably good growth and gave evidence of nutritional well-being. No evidence was found that plants grown in an inorganic medium are deficient in any dietary essentials.

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# REDUCTION OF FERRIC HYDROXIDE BY STRAINS OF *BACILLUS POLYMYXA*<sup>1</sup>

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Iron, both free and in various stages of hydration, occurs in soils in combination with organic and siliceous materials and as oxides. In most arable soils virtually all of the iron remains in the oxidized condition. When anaerobic conditions are established in soils, considerable reduced iron may accumulate. Ferrous compounds generally are more soluble than ferric compounds and hence are commonly mobilized to regions favorable for their reoxidation, where they are precipitated. Accumulation of iron in plants, pipes, subsoils, and bogs is of considerable economic importance.

According to present concepts, the reduction of iron oxides and hydroxides in soil is due principally to microbiological activity. Starkey and Halvorsen (6) have shown clearly the role of the microflora in altering conditions which determine the equilibrium between ferric and ferrous ions.

Strains of *Bacillus polymyxa* that are exceptionally active in reducing ferric oxide and ferric hydroxide recently have been isolated from soil. This paper is a brief report of the isolation, identification, and activity of these strains.

## EXPERIMENTAL

### *Isolation of cultures*

A 500-gm. sample of clay from the subsoil under Miami silt loam was added to a solution of 4,750 ml. of distilled water and 250 ml. of 0.2 *N* NaOH. The suspension was shaken vigorously for a few minutes and strained through cheesecloth to remove large particles. It was further dispersed in a Waring Blender for 30 seconds and divided equally among five 2-liter beakers, from which the supernatant suspension was decanted after 3 hours. The resulting suspension of colloids was at pH 7.8 and quite stable. The suspension was sterilized with steam under 15 pounds pressure for 30 minutes just before use, and sterile glucose solution was then added aseptically to give a final concentration of 0.5 per cent. When a solid medium was desired, 2 per cent of agar was added prior to sterilization.

When this medium was inoculated with soil and incubated at 30°C. for 4 to 7 days, the suspension turned blue as a result of the reduction of ferric oxides surrounding the colloids (1). When streak plates of the same medium were prepared and incubated anaerobically at 30°C. for 1 week, colonies developed which caused a blue discoloration of the medium. After a second streaking, colonies were picked to peptone-glucose agar slants. When reinoculated into soil colloid-

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glucose broth, these cultures caused a strong reduction of ferric oxides in 2 to 3 days.

Seven cultures were isolated by this technique from three soils from various parts of Indiana.

### *Identification of cultures*

All cultures isolated were facultative aerobic bacilli, produced endospores, and fermented glucose with the production of gas and 2,3-butylene glycol. All are considered to be strains of *B. polymyxa*. Two cultures were selected for detailed study. These cultures differed slightly with respect to the type of growth in peptone-glucose broth but were found to be identical in all other respects. Only one culture, designated as # 14, is described, as follows:

*Spores.* The spores are ovoid, borne centrally, and are about  $2\mu$  by  $1\mu$ , sometimes with tabs. The spores swell to about  $3.5\mu$  by  $1.7\mu$  before germination, which generally is polar.

*Sporangia.* The sporangia are medially swollen clostridia containing granulose when grown on potato-dextrose broth.

*Rods.* The first cells appearing after germination of the spore on potato-dextrose agar are swollen and irregular. In older colonies, cells are about  $5\mu$  by  $0.7\mu$ . Chains of four or five cells are sometimes found in liquid media.

*Nutrient gelatin without carbohydrate.* There is no liquefaction after 30 days. Growth is extremely slight.

*Peptone-glucose agar slant.* Growth is moderate, translucent, viscid, becoming membranous and adherent with age. No pigment is produced. There is virtually no growth if glucose is omitted.

*Peptone-glucose broth.* The medium becomes turbid, with some sediment. No pellicle or ring is formed.

*Litmus milk.* Little acid is produced and the litmus is reduced but no coagulation occurs.

*Fermentation of carbohydrates.* Glucose is fermented with the production of 2,3-butylene glycol, acetoin, ethyl alcohol, acetic acid, formic acid, lactic acid,  $\text{CO}_2$ , and  $\text{H}_2$ . Acid and gas are produced from sucrose, mannose, maltose, dextrin, mannitol, and starch. Acid is produced from sorbitol, amygdalin, and lactose. There is no visible action on aesculin, glycerine, rhamnose, arabinose, and xylose. With the exception of glucose, tests with all carbohydrates were made in nutrient agar (0.5 per cent agar) containing bromthymol blue and the carbohydrate.

*Other characteristics.* Neither indol nor  $\text{H}_2\text{S}$  is produced. Nitrates are not reduced to nitrites. Catalase is produced.

*Optimum temperature.* Between 30 and 35° C.

*Distinctive characteristic.* Iron as ferric oxide or hydroxide is rapidly reduced.

### *Reduction of iron on soil colloids*

Two hundred and sixty-five cultures were tested for their ability to reduce iron on soil colloids with glucose as the source of energy. The tests were made in the soil colloid medium described previously. The cultures tested included 250 unidentified species of yeasts, actinomycetes, and bacteria recently isolated from soil; two cultures of *Aerobacter aerogenes*; one culture of *B. macerans*; three cultures of *B. polymyxa* from the A.T.C.C. (nos. 7047, 840, and 7070); two enrichment cultures of *Clostridium* sp.; and seven strains of *B. polymyxa* isolated as described above. Excepting the isolated cultures of *B. polymyxa* and one en-

richment culture of *Clostridium* sp., none of the cultures reduced sufficient iron to discolor the soil colloid-glucose medium or to give more than a faint test with potassium ferricyanide after 2 weeks' incubation at 30°C. The cultures of *B. polymyxa* isolated as described above reduced 84 to 153 mgm. of iron within 24 hours, and the enrichment culture of *Clostridium* sp. reduced 5 mgm. of iron in 24 hours. It is not known whether this iron was reduced by the *Clostridium* sp. itself or by contaminants which were present in small numbers.

With the soil colloid-glucose broth as a selective medium, the number of cells per gram of soil which were capable of exceptional reduction of iron was determined by the dilution technique to vary from 10,000 to 100,000 in samples of six soil types.

#### *Dissimilation of glucose in presence of ferric hydroxide*

A little preliminary quantitative work was done to find out something about the mechanism by which these cultures so rapidly reduced ferric hydroxide. Although this objective was not fully achieved, some of the observations made are of sufficient interest to justify inclusion here.

Two media were used for quantitative studies. One medium contained 1.0 per cent Bacto peptone and about 2.4 per cent glucose (c.p.). The other contained 0.31 per cent  $K_2HPO_4$ , 0.08 per cent  $KH_2PO_4$ , 0.02 per cent KCl, 0.02 per cent  $MgSO_4 \cdot 7H_2O$ , 0.5 per cent asparagine, and about 2.4 per cent glucose.

The culture container consisted of two 500-ml. Erlenmeyer flasks, each provided with a side arm and connected at the necks with an h-shaped glass tubing. One hundred and fifty ml. of medium containing ferric hydroxide, when this was desired, was put into one flask and sterilized. Fifty ml. of sterile glucose solution was then added through the side arm. About 300 ml. of 3 per cent  $Ba(OH)_2$  was put into the second flask. In each instance, the media were inoculated with 1 ml. of a peptone-glucose broth culture of *B. polymyxa* #14 incubated 24 hours at 35°C. After inoculation, the side arm of both flasks and the upper open end of the h-shaped tube connecting the flasks were drawn out to capillary size and sealed.

Ferric hydroxide suspension was prepared by dialyzing the material thrown down by slowly adding fresh KOH solution in excess to a solution of ferric chloride. This suspension did not give an immediate positive test for ferrous ion or ferric ion with potassium ferrocyanide or potassium ferricyanide. The pH of the suspension was 7.8. Ferric hydroxide settled slowly on standing.

After 7 days of incubation at 35°C., the inoculated culture medium was analyzed for certain products of fermentation. Rubber tubing was placed over the capillary tips of the various side arms, which were then broken, and gases not absorbed by the  $Ba(OH)_2$  were forced into an Orsatt gas analyzer by filling both flasks with boiled distilled water. Carbon dioxide was determined volumetrically by absorption in 10 per cent KOH. Hydrogen was determined by combustion. The diluted culture was made up to exactly 600 ml., and a 100-ml. aliquot was acidified with  $H_2SO_4$ , boiled, and the gases evolved were analyzed. Carbon dioxide absorbed by the  $Ba(OH)_2$  was determined by weighing the  $BaCO_3$  pro-

duced. The carbonate was washed rapidly with boiled distilled water on a Büchner funnel. Carbonate and filter paper were put into a Gooch type crucible with a sintered glass bottom and dried for 2 hours at 110°C. The crucible was then weighed, the carbonate washed out with dilute HCl, the crucible dried again, and the loss in weight determined.

Original and residual sugar concentrations were determined by the method of Stiles, Peterson, and Fred (7).

TABLE 1

*Influence of ferric hydroxide on dissimilation of glucose by strains of B. polymyxa*

DISSIMILATION PRODUCT FOUND	AMOUNTS OF PRODUCTS IN FERMENTATIONS TREATED AS INDICATED									
	Synthetic medium*						Organic medium†			
	No Fe(OH) <sub>3</sub>		Fe(OH) <sub>3</sub> added		Na-acetate		No Fe(OH) <sub>3</sub>		Fe(OH) <sub>3</sub> Added	
	mgm./100 ml.	moles/100 moles glucose	mgm./100 ml.	moles/100 moles glucose	mgm./100 ml.	moles/100 moles glucose	mgm./100 ml.	moles/100 moles glucose	mgm./100 ml.	moles/100 moles glucose
Glucose fermented.....	1029		2333		2301		1334		2380	
Acetic acid added.....	0	0	0	0	275	36.8	0	0	0	0
Carbon dioxide .....	502	199	968	170	919	163	606	186	1036	178
Hydrogen.....	5.9	51	8.1	31	1.3	5	7.9	53	8.8	33
Formic acid.....	29	11	72	12	98	17	30	9	73	12
Lactic acid.....	28	17	220	19	14	1	95	14	88	7
Ethyl alcohol.....	190	72	488	82	403	68	265	78	570	94
Acetoin.....	11	0.5	12	1	11	1	7	1	24	2
2,3-butylene glycol ...	331	64	594	51	907	79	328	49	522	44
Acetic acid.....	0	0	0	0	0	0	0	0	0	0
Iron reduced.....			303	42					454	61
C—recovery .....	112.1		101.8		95.3		98.8		97.2	
Redox index‡.....	1.06		1.00		0.905		1.06		1.03	

\* 0.31 per cent  $K_2HPO_4$ , 0.08 per cent  $KH_2PO_4$ , 0.02 per cent KCl, 0.02 per cent  $MgSO_4 \cdot 7H_2O$ , 0.5 per cent asparagine, 2.4 per cent glucose (c.p.)

† 1.0 per cent Bacto peptone, 2.4 per cent glucose (c.p.)

‡ Oxidized  
Reduced

Ethyl alcohol was determined by distilling 75 per cent of an aliquot of alkaline culture through a short Vigreux-type column, and oxidizing the alcohol with potassium bichromate. The acid produced was separated by steam distillation and titrated. The distillation constants of the acid in the steam distillate were almost identical with constants for pure acetic acid.

Volatile acids were determined by acidifying a portion of culture with  $H_2SO_4$  (blue to Congo red) and distilling with steam. Distilling constants of the acids in the steam distillate indicated that formic acid was the only acid present in completed fermentations, although acetic acid was found in the early stages of fermentation.

The residue from the steam distillation of volatile acids was extracted continuously with ether for 48 hours, and lactic acid in the extract was determined by the method of Friedemann and Graesser (2). In preliminary trials, lactic acid found was sufficient to account for total nonvolatile acids. Hence lactic acid was presumed to be the only nonvolatile acid present in appreciable amounts.

Acetoin was determined by the method of Langlykke and Peterson (3).

The 2,3-butylene glycol was separated from the slightly alkaline medium by extracting continuously with ether for 48 hours. Glycol in the extract was determined by oxidizing 10 ml. or less of extract with 25 ml. of 0.01 *M* KIO<sub>4</sub> and 5 ml. of *N* H<sub>2</sub>SO<sub>4</sub>. Acetaldehyde produced was distilled directly into 1.25 per cent NaHSO<sub>3</sub> solution, and the bisulfite released by subsequent addition of NaHCO<sub>3</sub> was titrated with 0.01 *N* iodine.

Five fermentations are reported. Two of these were in the organic medium, one with and one without ferric hydroxide. Three were in the synthetic medium, one with ferric hydroxide added, one with sodium acetate added, and one with nothing added. The amounts of end products found in the fermentations are shown in table 1.

#### DISCUSSION OF RESULTS

The type and amount of end products produced suggests that dissimilation of glucose by these strains of *B. polymyxa* follows a course similar to that of *Aerobacter indologenes*.

According to Reynolds and Werkman (5), *A. indologenes* produces a 3-carbon intermediate which is oxidized to pyruvic acid in conjunction with reduction of acetic acid, acetaldehyde, or 2,3-butylene glycol. Pyruvic acid may be reduced to lactic acid, form formic and acetic acids as paired products, or form acetaldehyde and CO<sub>2</sub> as paired products. Formic acid may split into carbon dioxide and hydrogen gas.

If *B. polymyxa* #14 dissimilates glucose in this manner, then the 3-carbon intermediate, molecular hydrogen, or formate is the most probable hydrogen donor by which ferric hydroxide might be reduced. Resting cells of *B. polymyxa*, washed twice in Ringer's solution and suspended in 2 ml. of phosphate buffer (pH 7.2), together with 1 ml. of ferric hydroxide suspension and 1 ml. of  $\frac{1}{2}$  *M* glucose, do actively reduce iron. If the glucose is omitted or the cells are boiled, then no reduction of iron occurs. All attempts to replace glucose with dilute solutions of sodium formate or with hydrogen gas washed with silver nitrate, alkaline pyrogallol, and water have failed. Unfortunately pure dihydroxyacetone, glyceraldehyde, and methyl glyoxal had not been obtained at the time this work was interrupted. Impure solutions of these intermediates prepared by oxidation of glycerol with either bromine or hydrogen peroxide and ferrous sulfate according to Neuberg and Hofmann (4), were found to reduce considerable ferric hydroxide at pH 7.0 in 1 hour at 37°C., even in the absence of cells.

In the presence of ferric hydroxide, glucose was fermented very much more rapidly than in its absence. Also the amount of hydrogen produced per mole of glucose fermented was less when ferric hydroxide was present, and the ratio of



ethyl alcohol to 2,3-butylene glycol was widened somewhat. Acetate disappeared when added to the fermenting culture and could be recovered almost quantitatively as 2,3-butylene glycol. Acetate, like iron, increased the fermentation rate and decreased the amount of hydrogen produced per mole of glucose fermented.

#### SUMMARY

Strains of *B. polymyxa* have been isolated which rapidly reduce ferric hydroxide in suspensions and/or on soil colloids. Cells of such strains occur in relatively large numbers in soil samples tested. Preliminary biochemical studies have shown that in the presence of ferric hydroxide (or sodium acetate), glucose is more rapidly fermented and less hydrogen is produced. These studies have not revealed the process by which iron is reduced.

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# RELEASE OF ADSORBED K, Ca, Mg, AND Ba FROM A SOIL COLLOID AS INFLUENCED BY THE NATURE OF THE ACIDOID LINK<sup>1</sup>

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A previous series of contributions (4, 5, 6) pointed out that the removal of the free oxides of iron and aluminum from soil colloids markedly affected certain of their properties. During the progress of these studies, observations made in connection with electrodialysis and salt-exchange reactions of colloids that had been phosphated led to the belief that the release of adsorbed cations from exchange material is related to the type and nature of the acidoid linkage in the colloid. Unfortunately, this investigation had to be discontinued shortly after it had progressed past the initial stages. Recently, however, the study was again undertaken and now has been completed. Between these periods it seems to have been shown that the release of adsorbed cations is a function of the nature and type of secondary clay mineral present in the colloidal fraction of soils (1).

It is the purpose of this paper to point out that the release of adsorbed K, Mg, Ca, and Ba ions from a soil colloid is related to the nature of the bonding type of acidoid linkage in the soil colloid.

## EXPERIMENTAL METHODS

For the study here reported, the colloidal fraction of the B horizon of Sassafras loam was isolated and used. The location, sampling site, and analyses of this colloid were previously reported (4).

Variations in the nature and type of bonding acidoid linkages were obtained by precipitation of the colloidal fraction at the isoelectric point with phosphate, silicate, or humate ions. Approximately 200 gm. of the electrodialyzed colloid was suspended, by mechanical stirring, in 4 liters of distilled water containing phosphate ( $\text{H}_3\text{PO}_4$ ), silicate ( $\text{Na}_2\text{SiO}_3 + \text{HCl}$ ), or humate ( $\text{Na humate} + \text{HCl}$ ) ions. The suspensions were allowed to stand overnight, and the following morning the precipitated floc was transferred to a large funnel and washed with 2 liters of *N* neutral  $\text{NH}_4\text{Ac}$  then with distilled water to remove the excess of the reagent. The sample was then air-dried and aliquoted for the preparation of cation-saturated colloids. In later discussions in this paper, the phosphated, silicated, and humated colloids are designated as "treated" colloids to differentiate them from the "untreated" colloids.

The homionic colloids were prepared by leaching samples with 8 liters of the *N* neutral acetate of Ca, Mg, Ba, and K, respectively; then adding the respective chlorides of the cations. The excess salts were removed from the samples by washing the Ca, Mg, and Ba samples with distilled water and the K samples with

<sup>1</sup> Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

50 per cent ethyl alcohol until free of chlorides. The chloride-free samples were air-dried and ground to pass a 40-mesh sieve. The adsorbed-cation contents were then determined by analyses of solutions resulting from leaching the samples with 0.05 *N* HCl.

In the conductivity tests, 4 gm. of untreated colloids or quantities of treated samples containing equivalent quantities of adsorbed cations were suspended in 50 ml. of CO<sub>2</sub>-free water and allowed to stand for predetermined periods of 1 day, 2 weeks, or 4 weeks. At the end of these periods, conductivity tests on the clear supernatant liquids were made with a Freas conductivity cell and a Wheatstone bridge arrangement.

The electrodialysis studies were conducted with Mattson cells, using a uniform current intensity of 0.4 ampere for 24 hours. The size of the electrodes and the distance between them were constant in all tests. At the end of this time, the cathode compartment of the cell was drained and flushed thoroughly with 2 *N* HCl to render soluble any of the precipitated ions. The cathode parchment paper was also subjected to this treatment. The cathode dialyzates were analyzed by standard methods for the respective cations after the removal of interfering ions.

The exchange studies were performed by suspending either 3 gm. of the untreated colloids or quantities of treated colloids with cation content equivalent to that of the untreated samples, in 200 cc. of solution containing either half or the whole symmetry concentration of HCl. The samples were allowed to stand for 3 days at room temperature with intermittent shaking, after which aliquots of the supernatant liquid were analyzed for the several cations by the methods previously mentioned.

The pH values in all tests were obtained by the use of a glass-electrode potentiometer system either in clear supernatant liquids or in suspensions.

#### ADSORPTION OF ANIONS AND CATIONS BY THE SASSAFRAS COLLOID

The adsorption of silicate, phosphate, and humate ions by the Sassafras colloid and the pH values of the isoelectric precipitation are presented in table 1. The latter values were arrived at by extrapolation of cataphoretic measurements during the investigation of another series of experiments with this colloid.

The relation between the treatments of the colloid, the exchange capacity of the untreated and treated samples with Ca, Ba, Mg, and K, the number of new exchange positions formed as the result of the treatments, and the pH values of suspensions of the cation-saturated colloids are presented in table 2.

Several facts of interest are to be noted from the data in table 2. The most important of these is that the order of cation adsorption by the various treated colloids is generally influenced by the treatment. The order of cation adsorption by the untreated and the humated colloid, which is considered to be normal, is: Mg > Ba > Ca > K. A reversal in the order of Ba and Mg with the phosphated colloid and of Ca and K with the silicated colloid should be noted. The order of cation adsorption by the untreated colloid was previously noted (5).

The increases in exchange capacity for the treated colloids vary with the nature

of the replacing cation. The reasons for these increases have been discussed (2, 3). No correlation exists between the quantity of any specific cation retained by the exchange material, the percentage increases in exchange capacity, and the number of new bonding linkages formed as the result of the various treatments.

The pH values of suspensions of the cation-saturated clays show several points of interest. When comparisons are made of the untreated colloids, on an equal-weight basis, the order for pH values of the suspensions is  $K > Ba > Mg > Ca$ . When comparisons are made between the various treatments for any specific cat-

TABLE 1  
*Adsorption of anions by Sassafras loam colloid*

TREATMENT	ANION ADSORBED/GM.	pH SUPERNATANT LIQUID
Phosphate.....	0.12 m.e.	2.65
Silicate.....	7.00 m.e.	2.85
Humate.....	1.12 gm.	2.00

TABLE 2  
*Exchange capacity and ph values of cation-saturated colloids*  
Exchange capacity and bonds, per 100 gm.

TREATMENT	EXCHANGE CAPACITY				EXCHANGE CAPACITY PERCENTAGE INCREASE				NEW EXCHANGE BONDS MOLECULES ( $10^{10}$ )				pH*			
	Ca	Ba	Mg	K	Ca	Ba	Mg	K	Ca	Ba	Mg	K	Ca	Ba	Mg	K
	m.e.	m.e.	m.e.	m.e.												
None																
Equal weights.....	22.97	24.33	33.40	22.68	....	....	....	....	....	....	....	....	7.30	7.50	7.40	8.15
Equivalent cation contents.....	..	..	..	..	....	....	....	....	....	....	....	....	7.35	7.30	7.40	8.15
Phosphated.....	34.06	42.54	40.41	28.32	48.3	74.8	20.9	20.3	326	552	212	342	7.45	7.65	7.40	7.95
Silicated.....	28.72	35.04	36.46	32.59	25.0	44.0	9.7	43.8	174	325	98	650	7.55	7.50	7.40	8.50
Humated.....	86.64	89.54	96.30	64.04	277.1	268.0	189.9	182.4	1928	1977	1925	2712	7.60	7.50	7.55	7.75

\* Suspensions, 24 hours' contact.

ion, at equivalent ion contents, it will be noted that with Ca, the order of pH values of the suspensions is: phosphated < silicated < humated. Similarly with Ba, Mg, and K ions the respective orders are: silicated = humated < phosphated; phosphated = silicated < humated; and humated < phosphated < silicated.

#### CONDUCTIVITY MEASUREMENTS OF CATION-SATURATED COLLOIDS

The evaluation of conductivity data concerned with the measurements of suspensions is extremely difficult. In this study, therefore, the measurements were confined to the clear supernatant liquids of the various colloidal systems. Table 3 contains data on the conductivity of the supernatant liquid at two time intervals, as well as pH measurements at these same time intervals.

The influence of the bonding linkages upon the dissociation of Ca, Mg, Ba,

and K is strongly shown when comparisons are made between the conductivity of the supernatant liquids of the treated colloids and that of the untreated. With the exception of the Ba-phosphated colloid and the K-silicated colloid, the conductivity of the supernatant liquid of the treated colloid saturated with Ca, Mg, K, or Ba ions is greater than that of the untreated colloids. This would indicate that the hydrolysis of the cation-saturated colloids that were either phosphated,

TABLE 3  
*Conductivity and pH values of cation-saturated colloids at varying time intervals*

TREATMENT	pH					CONDUCTIVITY SUPERNATANT	
	Supernatant		Suspensions			2 weeks	4 weeks
	2 weeks	4 weeks	1 day	2 weeks	4 weeks		
						$10^{-6}$ ohms	$10^{-6}$ ohms
<i>Ca</i>							
None.....	7.25	6.50	7.30	7.35	7.00	85.6	135.5
Phosphated.....	7.00	6.85	7.45	7.00	6.95	171.5	239.8
Silicated.....	6.95	6.85	7.55	7.15	7.10	110.6	154.5
Humated.....	7.05	7.00	7.60	7.30	7.25	99.4	125.6
<i>Ba</i>							
None.....	6.80	6.80	7.50	7.55	7.15	83.4	124.7
Phosphated.....	7.00	6.90	7.65	6.95	6.60	83.4	126.1
Silicated.....	7.05	6.50	7.50	7.20	6.80	102.0	137.2
Humated.....	6.70	6.70	7.50	6.95	7.00	117.0	163.6
<i>Mg</i>							
None.....	7.35	7.45	7.40	7.40	7.55	62.9	104.5
Phosphated.....	7.15	7.20	7.40	7.15	7.20	168.0	228.6
Silicated.....	7.00	7.20	7.40	7.20	7.50	116.0	187.9
Humated.....	6.85	7.20	7.50	7.15	7.55	132.0	201.7
<i>K</i>							
None.....	7.55	8.00	8.15	7.60	8.05	214.0	311.8
Phosphated.....	7.45	7.15	7.95	7.45	7.35	376.0	480.0
Silicated.....	7.70	7.80	8.50	7.70	8.05	208.0	267.9
Humated.....	7.45	7.45	7.75	7.45	7.50	638.0	1075.0

silicated, or humated is greater than that of the untreated colloid. The conductivity of the supernatant liquid of all the systems increases with time. For example, with the Ca-phosphated colloid, the conductivity is  $171.5 \times 10^{-6}$  and  $239 \times 10^{-6}$  ohms, respectively.

Another interesting fact to be noted from the data in table 3 is that the pH values of the suspensions for the Ca, Ba, and K series, in general, decrease with increasing time intervals whereas with most of the Mg series the pH increases

with time. Similarly, the pH values of the supernatant liquid in the Ca and Ba systems decrease or remain fairly uniform with increasing time, while with all the Mg series and two of the four K series, the pH increases with time.

The pH values of the suspensions of the systems are generally greater than the pH value of the supernatant liquid. The maximum difference in pH is 0.5 unit, noted with the Ca-untreated colloid. In most cases, however, the difference is approximately 0.3 pH unit.

If comparisons are made of the conductivity of the supernatant liquid of the untreated colloid with the several ion saturations, on an equal-weight basis, the clays can be arranged in the following order:  $K > Ca > Ba > Mg$ . When com-

TABLE 4  
*Conductivity and pH values of untreated colloids at equivalent cation contents*

CATION	pH*			CONDUCTIVITY†	
	1 day	2 weeks	4 weeks	2 weeks	4 weeks
				<i>10<sup>-4</sup> ohms</i>	<i>10<sup>-4</sup> ohms</i>
Ca.....	7.25	6.60	6.95	168.0	185.4
Ba.....	7.30	6.50	7.30	85.7	124.7
Mg.....	7.40	6.45	7.45	85.7	130.7
K.....	8.15	7.60	8.05	214.0	311.8

\* 1:1.5 suspensions.

† Supernatant liquid.

TABLE 5  
*Release of cations by hydrolysis\**

TREATMENT	Ca	Ba	Mg	K
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
None.....	16.4	9.0	26.2	20.2
Phosphated.....	21.9	4.8	32.3	29.3
Silicated.....	19.8	7.4	33.6	11.3
Humated.....	16.4	9.0	37.6	32.1

\* Time interval, 4 weeks.

parisons are made on equivalent cation contents (see table 4) the order is  $K > Ca > Mg = Ba$ , the position of the latter two cations varying slightly.

The quantity of cations hydrolyzed from the clays at the end of the 4-week period was determined by analysis of the supernatant liquid. The results are presented in table 5. For the untreated colloid, the order of hydrolysis of the cations is:  $Ba < Ca < K < Mg$ . For the K series of colloids the order is: humated  $>$  phosphated  $>$  silicated. Similarly for the Ca, Ba, and Mg colloids, respectively, the order is: phosphated  $>$  silicated  $>$  humated; humated  $>$  silicated  $>$  phosphated; and humated  $>$  silicated  $>$  phosphated. The conductivity data for the untreated colloid and the quantity of cations hydrolyzed are not in agreement. For example the order for increasing conductivity for the

untreated colloid is: Mg, Ba, Ca, K, while the order for increasing hydrolysis is: Ba, Ca, K, Mg. The reasons for this discrepancy may lie in the fact that the conductivity of the supernatant liquid represents the net conductivity of all the

TABLE 6  
*Cation, silica, and  $R_2O_3$  contents of hydrolyzates*

CATION	TREATMENTS	CATION	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>
		<i>m.e.</i>	<i>mgm.</i>	<i>mgm.</i>
Ca	None	0.3024	13.0	1.5
	Phosphated	0.4032	7.0	0.5
	Silicated	0.3528	6.0	1.5
	Humated	0.3024	4.5	0.5
Ba	None	0.1708	7.0	4.0
	Phosphated	0.0940	12.0	7.0
	Silicated	0.1452	9.0	5.0
	Humated	0.1708	5.0	0.5
Mg	None	0.7020	25.0	4.0
	Phosphated	0.8640	4.0	0.0
	Silicated	0.9000	4.0	0.0
	Humated	1.0080	16.0	1.2
K	None	0.3600	115.0	5.0
	Phosphated	0.6736	75.0	4.0
	Silicated	0.2964	18.0	1.0
	Humated	1.6480	260.0	2.0

TABLE 7  
*Effect of nature of colloids on hydrolysis of cations*

NAME	CATION-EXCHANGE CAPACITY*				PERCENTAGE OF TOTAL CATIONS HYDROLYZED				pH†			
	Ca	Ba	Mg	K	Ca	Ba	Mg	K	Ca	Ba	Mg	K
	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>								
Colts Neck‡.....	13.4	14.3	14.5	9.5	11.7	1.7	10.8	8.9	7.50	7.30	7.40	7.75
Dutchess‡.....	13.9	12.6	13.1	12.1	6.7	3.3	16.5	4.8	7.10	6.30	7.00	7.40
Sassafras§.....	22.9	24.3	33.4	22.7	16.4	9.0	26.2	20.2	7.30	7.50	7.40	8.15

\* Per 100 gm.

† 1:1.5 suspensions.

‡ 3-day hydrolysis period.

§ 4-week hydrolysis period.

ions in solutions. Analysis of the supernatant liquid for cations, SiO<sub>2</sub>, and R<sub>2</sub>O<sub>3</sub>, the results of which are presented in table 6, shows wide variations in SiO<sub>2</sub> and R<sub>2</sub>O<sub>3</sub> contents. Conductivity data, therefore, even for the clear supernatant liquid of colloidal systems, must be interpreted with care.

The hydrolysis data for the K, Ca, and Mg systems of the treated colloids,

which are presented in table 5, indicate that, except for the K-silicated and the Ca-humated treatments, hydrolysis is greater for the treated colloids than for the untreated series. Data on the Ba series of the treated colloids, however, indicate decreased hydrolysis of the cation for the phosphated and silicated series and equivalent hydrolysis for the humated series when the systems are compared with the untreated series. It is surprising to note that the hydrolysis of adsorbed Mg is greater than that of K, Ca, or Ba, irrespective of the treatment of the colloid. Data on the quantity of Mg electrodialed per unit time under standard conditions and those on the replacement of adsorbed Mg by H ions, however, do not follow the hydrolysis data.

Since it has been pointed out (1) that the nature of the secondary clay minerals present in the colloidal fraction of soils affects the degree of hydrolysis of adsorbed cations, two samples of colloids utilized in previous work were re-examined by the technique employed in this study. The results of this test are presented in table 7. The Colts Neck colloid seems to release approximately the same amounts of Mg and Ca by hydrolysis, whereas the Dutchess colloid releases approximately two and one-half times as much Mg as Ca. It would seem, from the data on the three colloids, that the release, by hydrolysis, of adsorbed Mg is at least as great as that of adsorbed Ca, Ba, or K.

#### REPLACEMENT OF ADSORBED Ca, Mg, Ba, AND K BY H IONS

The replacement of adsorbed Ca, Ba, Mg, and K ions by H ions (HCl) from the various treated clays, at equivalent cation contents, was determined at half and at the whole symmetry concentration of H ions. The results are presented in table 8.

The order of cation release for the untreated colloid at half the symmetry concentration is:  $K > Ca > Mg > Ba$ . The order is identical at the whole symmetry concentration, but the percentages released are higher. The influence of the new bonding linkages upon the release of adsorbed ion is indicated by the increased release of specific cations in certain series of treatments. For example, with the K colloids, the order of release of K for the  $\frac{1}{2}$  symmetry concentration is: humated > phosphated > silicated > untreated. With Ca, Mg, and Ba the respective orders are: phosphated > untreated = silicated > humated; phosphated > humated > untreated > silicated; and phosphated > humated > untreated > silicated. At the symmetry concentration of HCl for the K colloids, the order for the treatments is identical to that of the half symmetry values. With the Ca, Mg, and Ba colloids, at symmetry concentrations, shifts occur in the order. It is possible that these shifts are related to the solubility effect of HCl, which probably ruptures the bonding linkages formed as the result of the treatments. This effect is especially marked in the Ca-phosphated colloid where approximately 98 per cent of the adsorbed Ca is released at the symmetry concentration of HCl. With the exception of the Ca-series of the silicated and humated treatments, the result of phosphating, humating, and silicating colloids is an increased release of adsorbed Ca, Mg, Ba, and K, over that of the untreated colloid. The significance of this point will be discussed later.



It is of interest to compare the quantities of cations that are hydrolyzed from the colloids with the amounts released from the clays by the half and the whole symmetry concentration of HCl (*cf.* tables 5 and 8). With the K-series, half the symmetry concentration of HCl resulted in the release of an additional 34 to 67 per cent of the adsorbed K, depending upon the treatment. The symmetry concentration of HCl, on the same series, resulted in an additional release of approximately 0.6 to 39 per cent of the adsorbed ion, the magnitude of the release depending upon the treatment of the colloid. Similarly for the Ca, Ba, and Mg ions the quantities released amounted to: 33 to 37 per cent for half the symmetry value and 29 to 40 per cent for the symmetry value; 32 to 42 per cent for half the symmetry value and 30 to 33 per cent for the symmetry value; and 13 to 22 per cent for half the symmetry value and 21 to 35 per cent for the symmetry value, respectively. It is interesting to note that for the Ca and Ba ions, the additional release of these ions by half the symmetry value of H ions is fairly uniform and

TABLE 8  
*Release of adsorbed cations by H<sup>+</sup> (HCl)*

TREATMENT	Ca		Ba		Mg		K	
	‡ Sym- metry Concen- tration	Sym- metry* Concen- tration	‡ Sym- metry Concen- tration	Sym- metry Concen- tration	‡ Sym- metry Concen- tration	Sym- metry Concen- tration	‡ Sym- metry Concen- tration	Sym- metry Concen- tration
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
None.....	53.4	85.1	42.1	72.6	48.3	74.3	54.4	93.7
Phosphated.....	57.4	97.7	47.1	80.4	54.7	78.4	64.7	100.0
Silicated.....	53.4	83.1	41.6	74.0	46.0	81.0	58.3	95.0
Humated.....	51.4	84.2	43.3	74.3	53.3	75.8	98.6	99.2

\* Symmetry concentration = H-ion concentration equivalent to cation content.

amounts to approximately 29 to 42 per cent. Increasing the H-ion concentration to the symmetry value gives approximately the same value. The values for identical concentration of H ions with K are somewhat irregular, but for Mg, the values are somewhat lower ranging between 13 and 22 per cent.

#### RELEASE OF ADSORBED CATIONS BY ELECTRODIALYSIS

The release of adsorbed Ca, Ba, Mg, and K from the colloids under standard conditions and a set period of electrodialysis is shown in table 9. The quantities of the cations not electrodialyzed but displaceable by leaching with 0.05 *N* HCl are also shown in this table.

Under the conditions of the test, the cations can be arranged in order of release by electrodialysis from the untreated colloid as follows: Mg < Ba < Ca < K. The order of release from the phosphated colloid is: Mg < Ba < K < Ca. From the silicated and humated colloids, respectively, the order of release is: Mg < Ca = Ba < K and Mg < Ca < Ba < K.

Irrespective of the individual effects of any specific treatment, the results indicate that the release of Ca, Ba, Mg, and K from the treated colloids is greater than that from the untreated colloid.

The Mg series of colloids exhibit several interesting effects. If the assumption is made that the release of Mg by electrodialysis is related to the solubility of the phosphate, silicate, and humate salts of Mg, the order obtained is Mg-humate < Mg-silicate < Mg-phosphate. Why Mg-humate—and it is conceivable that we are dealing with this compound since Mg is adsorbed by the humate bond—should be more insoluble than the corresponding silicate is not clear. Leaching the residues, after electrodialysis, with 0.05 *N* HCl tends to release additional Mg from the humated colloid but the total recovery is still less than that for the phosphated or the silicated colloid.

TABLE 9  
*Release of adsorbed cations by electrodialysis*

	CATION ELECTRODIALYZED				CATION DISPLACED (0.05 <i>N</i> )HCl				RECOVERY			
	Un-treated	Phos-phated	Sili-cated	Hu-mated	Un-treated	Phos-phated	Sili-cated	Hu-mated	Un-treated	Phos-phated	Sili-cated	Hu-mated
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Ca.....	86.4	98.4	92.6	88.6	6.2	1.6	4.0	3.2	92.6	100.0	96.6	91.8
Ba.....	78.1	91.7	92.0	94.5	8.2	4.9	5.9	2.6	86.3	96.6	97.9	97.1
Mg.....	45.4	80.8	73.0	65.0	17.8	16.2	20.4	14.0	63.2	97.0	93.4	79.0
K.....	94.9	96.8	96.6	98.4	5.1	3.2	3.4	1.6	100.0	100.0	100.0	100.0

#### DISCUSSION

The addition of phosphate fertilizers and organic matter to soils increases their exchange capacity and reduces their ultimate pH (2, 3, 4). It seems best to consider the increases in exchange capacity as due to the formation of new complexes that have exchange powers. The new complexes or formations may be due to reactions between soluble ions added and soluble ions present in the soil solution capable of forming insoluble salts. In addition, reactions between hydrated oxides of Fe and Al or an anion replacement between the anions added in solution and OH ions existing on the surfaces of the clay particles may be responsible for the formation of the new complexes.

From a theoretical consideration of the nature and reactions of these new formations, it is not logical to expect that the release of adsorbed cations will follow theories that have been developed for the release of cations from known secondary clay minerals (1). The evidence presented in this paper, although not clearly showing distinctions between bonding linkages of silicate, humate, and phosphate ion, definitely indicates that the introduction of new acidoid linkage into a soil colloid affects the release of adsorbed Ca, Mg, Ba, and K ions. The data on conductivity measurements, cation exchange by H ions, and electrodialysis substantiate this statement. It is believed, however, that differences exist between the acidoids when reactions initially occur in soils, especially in connection with the adsorption and release of cations. That the expected theoretical differences did not develop to a greater degree in this study is believed due to the drying treatments to which the colloidal material was subjected during its isolation and preparation.

The relative importance of the new formations in the soil depends upon the increases in exchange capacity resulting from the treatment. Since the laboratory investigation indicates that the degree of release of cations is altered in the new formations, studies are planned to note whether or not plants are capable of absorbing cations to a greater degree from soil material containing these new formations.

#### SUMMARY

The release of adsorbed Ca, Mg, Ba, and K from untreated, phosphated, silicated, and humated Sassafras loam colloid was studied by laboratory tests. The results indicate that:

1. The cation retention was influenced by the treatment. The normal order of cation retention was  $Mg > Ba > Ca > K$ . When the colloid was phosphated, the order was  $Ba > Mg > Ca > K$ ; and when silicated,  $Mg > Ba > K > Ca$ .

2. The conductivity of the supernatant liquid of the cation-saturated treated colloids was generally higher than that of the untreated colloidal systems at equivalent cation contents.

3. Hydrolysis of Ca, Mg, and K from the treated colloids was greater than from the untreated. With the Ba-systems, however, the hydrolysis was less. The hydrolysis of Mg was greater than that of K, Ca, or Ba, irrespective of the treatments of the colloid.

4. The cation order of replacement by H ions, at equivalent cation contents was:  $K > Ca > Mg > Ba$ . The percentage replacement of adsorbed Ca, Mg, Ba, and K by H ions was greater from the treated than from the untreated colloid.

5. The release of adsorbed Ca, Mg, Ba, and K ions by electrodialysis was greater from the treated than from the untreated colloids, under standardized conditions.

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# FIXATION OF POTASSIUM IN RELATION TO EXCHANGE CAPACITY OF SOILS: II. ASSOCIATIVE FIXATION OF OTHER CATIONS, PARTICULARLY AMMONIUM<sup>1</sup>

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In experiments previously reported, the authors (8) saturated samples of a Montalto colloid with Ba, Sr, Ca, Mg, and Na respectively in an attempt to fix these ions. The results were negative, corroborating the investigations of Chaminade and Drouineau (2), who intimated that Mg might be fixed in some cases. Page *et al.* (14, 15) maintain that all cations are fixed, the degree of fixation depending on the radius of the ion in question.

## FIXATION OF CA AND BA

In connection with the present study, a recheck was made on the possible fixation of Ca and Ba by bentonite and Montalto colloids. Both of these materials were used for the fixation of Ba, and hydrogen bentonite only was used for the fixation of Ca. The method of inducing fixation was similar to that previously reported (9).

TABLE 7  
*Fixation of calcium by bentonite*

	mgm.
Ca added to bentonite.....	42.7
Ca in leachate of fixed sample.....	57.6
Ca in leachate of water blank.....	14.4
Added Ca recovered.....	43.2
Ca fixed.....	0.0

Table 7 shows that Ca ions are not fixed. It should be pointed out that although the bentonite was hydrogen-saturated, there was also some Ca in the complex because of the grinding to which the mineral was subjected after saturation. This operation releases some of the elements originally present as part of the crystal structure, as shown by Kelley and Jenny (10). The difference between the Ca recovered and that added may be ascribed to experimental error.

Table 8 shows that Ba ions, likewise, are not fixed. The slight discrepancy between the amount of Ba added to the Montalto colloid and that recovered may be attributed to experimental error. In any event, it is insignificant when contrasted with the quantity of K that the colloid will fix under the same con-

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<sup>2</sup> Temporarily withdrawn; resubmitted September 12, 1946.

ditions. These results are quite divergent from those of Page (15), who reported that Ba fixation is of the same order of magnitude as K fixation. Nor does pedologic evidence support the idea of Ba fixation. If Ba were fixed it should accumulate somewhere in the profile of soils where Ba-bearing minerals are present in the parent material, and this phenomenon would have been noted. No such reports, so far as the authors could ascertain, are available.

TABLE 8

*Fixation of barium by mineral and soil colloids in comparison with fixation of potassium*

	H-BENTONITE*	MONTALTO H-COLLOID*
	m.e.	m.e.
Ba added.....	1.87	1.87
Ba recovered.....	1.87	1.84
Ba fixed.....	0.00	0.03
K fixed†.....	0.25	0.26

\* 2.344 gm. bentonite; 4.116 gm. Montalto colloid. These are symmetry quantities with respect to Ba added.

† Calculated from data of a different experiment using the same materials and fixed under the same conditions.

#### COMPARATIVE FIXATION AND RELEASE OF $\text{NH}_4$ AND K

Chaminade and Drouineau (2) in 1936 suggested fixation of  $\text{NH}_4$  and presented some data in support of this contention. While the work reported in the present paper was well under way, Chaminade (4) published some additional data relating to  $\text{NH}_4$  fixation. In neither of Chaminade's papers was the work extensive. It was therefore deemed desirable to investigate the comparative power of soils to fix  $\text{NH}_4$  and K.

By the way of a preliminary experiment, comparisons were run between fixation of K and  $\text{NH}_4$  by natural Wyoming bentonite. To each of four 5-gm. samples, 35 ml. of 0.1246 N KCl was added, and to each of four others, 35 ml. of 0.1249 N  $\text{NH}_4\text{Cl}$ . Two of the KCl-treated samples, together with sufficient water blanks, were alternately wetted and dried several times at 47°C. The other samples, and their water blanks, were handled in like fashion but at 74°C. After the fixing procedure, the systems were taken up with 0.05 N HCl, thrown on filters, and leached with acid of the same concentration. In the case of K, the filtrates were analyzed for that cation, and fixation was determined by the difference between K added and that recovered.  $\text{NH}_4$  fixation was determined directly by determining total nitrogen on the samples and on the blanks after sufficient leaching with acid. The difference was the  $\text{NH}_4$  fixed. Results are presented in table 9.

As is the case with K (3,7)<sup>3</sup>, it is noted that an increase in temperature causes an

<sup>3</sup> See also Levine, A. K. Relation of potassium fixation to the exchange capacity of soils. 1939 (*Unpublished Master's thesis*. Copy on file Rutgers University Library, New Brunswick, N. J.)

increase in  $\text{NH}_4$  fixed. The similarity with K in this case, however, appears to be merely qualitative. The reason for the lower fixation of  $\text{NH}_4$ , as compared with K at the same temperature, is not too readily explained. It is probable, however, in this instance at least, that the alkaline nature of the bentonite suspension contributed materially to the results obtained. As determined by thymol blue indicator, the pH of the natural bentonite suspension to which the  $\text{NH}_4\text{Cl}$  was added was more than 9.0. Under these circumstances, especially in view of the elevated temperature, it is undoubtedly true that appreciable quantities of  $\text{NH}_4$  were lost as volatile  $\text{NH}_3$ , and hence the amount of  $\text{NH}_4$  available for fixation was decreased.

In another series of experiments, hydrogen bentonite was substituted for natural bentonite and in addition Montalto hydrogen colloid (2  $\mu$  diameter and less, organic-matter-free) was used. To permit comparisons between the two fixing materials and between the two ions,  $\text{NH}_4$  and K, symmetry concentrations and simple multiples of these were used. These concentrations were worked out on the basis of exchange capacities of 0.43 and 0.86 m.e. per gram for the Montalto colloid and H-bentonite respectively. After the experiment was well

TABLE 9  
*Fixation of  $\text{NH}_4$  and K by natural Wyoming bentonite*

TEMPERATURE	$\text{NH}_4$ FIXED	K FIXED
$^{\circ}\text{C}.$	m.e.	m.e.
47	0.18	0.52
74	0.46	0.69

under way it was learned that the exchange capacity of the H-bentonite was not 0.86 (the value for the natural bentonite), but 0.73 m.e. per gram instead. The decrease was evidently due to the HCl treatment by which the bentonite was hydrogen-saturated. The difference in the exchange capacities is not so wide, however, that the interpretation of the results is seriously affected.

To separate 2.914-gm. samples of H-bentonite were added 10, 20, and 40 ml. of 0.1249 N  $\text{NH}_4\text{Cl}$ ; also to separate 5.869-gm. samples of Montalto H-colloid were added 10, 20, and 40 ml. of 0.1246 N KCl. These quantities were calculated to be one-half, one, and two times symmetry. Duplicate samples and blanks were then alternately wetted and dried five times at  $105^{\circ}\text{C}.$  (A check experiment showed that no  $\text{NH}_4$  was lost from an  $\text{NH}_4\text{Cl}$  solution dried at that temperature.) K fixation was determined as the difference between K added and that recovered;  $\text{NH}_4$  fixation was determined directly, as pointed out above.

The results in table 10 show marked likeness in the behavior of K and  $\text{NH}_4$  ions in the case of the Montalto colloid. Up through one symmetry concentration at least,  $\text{NH}_4$  and K are fixed in like amounts. This suggests that, with Montalto hydrogen colloid,  $\text{NH}_4$  and K are fixed in like manner. That these two ions enter with equal facility the exchange complex of some minerals is shown by Moller (13) and Schachtschabel (17). That  $\text{NH}_4$  should be fixed like K is not

surprising in the light of their similarities in many chemical properties, such electronic configuration and ionic diameters. The similarity of these ions in their physiologic reactions has been pointed out by Loeb (11).

With bentonite, however, there is no equivalence between  $\text{NH}_4$  and K fixed. In this instance the explanation offered to interpret the results of table 9 does not apply, for the pH of the hydrogen bentonite is far below neutral, being in the neighborhood of 4.2. Again, however, the work of Schachtschabel (17) can be brought to bear. Schachtschabel points out that although two cations may

TABLE 10

*Comparative fixation of ammonium and potassium by minerals and soil colloids*

RELATIVE CONCENTRATION OF ADDED ION	H-MONTALTO		H-BENTONITE		
	K fixed	$\text{NH}_4$ fixed	K fixed	K fixed (corrected*)	$\text{NH}_4$ fixed
	m.e.	m.e.	m.e.	m.e.	m.e.
$\frac{1}{2}$ Symmetry.....	0.29	0.29	0.20	0.24	0.10
1 Symmetry.....	0.37	0.36	0.32	0.38	0.18
2 Symmetry.....	0.68	0.44	0.54	0.64	0.23

\* Corrections are made by multiplying values in preceding column by 86/73.

TABLE 11\*

*Extraction of ammonium minerals with various chlorides*

EXTRACTING ION	AMMONIUM EXTRACTED†				
	$\text{NH}_4$ -muscovite	$\text{NH}_4$ -kaolinite		$\text{NH}_4$ -biotite	
	1.0N extraction solution	0.05N extraction solution	1.0N extraction solution	0.05N extraction solution	1.0N extraction solution
	per cent	per cent	per cent	per cent	per cent
Li.....	52.8	26.0	73.9	21.4	54.5
Na.....	67.2	26.1	75.4	24.2	66.0
Ca.....	51.7	46.8	76.0	31.1	51.5
Ba.....	64.0	47.4	76.4	37.6	63.5
H.....	97.3	38.0	74.2	36.1	99.3

\* After Schachtschabel (17).

† Expressed as per cent of total exchange capacity.

enter the exchange complex of one mineral in a given ratio, the ratio of entry may be altogether different with a different mineral. He presents numerous data to strengthen his assertion. It may be that the larger potassium fixation is explicable on the basis of greater entry, as compared with  $\text{NH}_4$ , into the complex in the case of hydrogen bentonite.

Schachtschabel saturated muscovite, kaolin, and biotite with  $\text{NH}_4$ . Separate samples of these ammonium minerals were extracted with solutions of various chlorides at different concentrations ranging from 0.05 N to 1.0 N. The extracts were then analyzed to determine the  $\text{NH}_4$  removed from the exchange complex.

The exchange capacities of the muscovite, kaolinite, and biotite used were 38.3, 7.76, and 32.6. m.e. per 100 gm. respectively. The data for 0.05 *N* and 1.0 *N* extracting solutions, collected from several of Schachtschabel's tables, are presented in table 11. They seem to substantiate the results obtained in our experiments. The quantities of  $\text{NH}_4$  extracted by normal HCl from muscovite and biotite far exceed those extracted by any of the other normal chloride solutions. With 0.05 *N* acid, however, no more  $\text{NH}_4$  was extracted than with some of the other ions. The results are readily explained on the basis of fixation of  $\text{NH}_4$ .

It was shown earlier (9) that when soil colloids containing fixed K are treated with normal HCl the fixed ion is released. Treatment with 0.05 *N* acid or with other cations does not accomplish this. The much higher values reported in table 11 for  $\text{NH}_4$  extracted from ammonium muscovite and ammonium biotite by normal acid than by other normal chloride solutions are accounted for on the basis of release of fixed  $\text{NH}_4$ . On the other hand, 0.05 *N* acid extracts only as much  $\text{NH}_4$  from ammonium biotite as do the other ions, because 0.05 *N* HCl is incapable of releasing appreciable quantities of fixed  $\text{NH}_4$ .

#### FIXATION OF $\text{NH}_4$ BY KAOLINITE AND BIOTITE

Work in this laboratory has shown that kaolinite fixes no K. It is then to be expected that the other ions, especially at higher concentrations, should extract just about as much  $\text{NH}_4$  from the exchange complex of kaolinite as does hydrogen. This is actually what occurs. The results for ammonium kaolinite and ammonium biotite are similar at 0.05 *N* concentration; this is as it should be, for at this concentration effects of release of  $\text{NH}_4$  fixed in biotite do not come into play. At the higher concentration, however, especially with hydrogen, the picture is different. In the cases of Li, Na, Ca, and Ba ions the percentage  $\text{NH}_4$  exchanged from biotite is less than that exchanged from kaolinite. This is explained on two counts: 1, less  $\text{NH}_4$  is available for exchange in the biotite system because of fixation; 2, with kaolinite,  $\text{NH}_4$  is exchanged on the surface (12) and hence is more readily removed by exchanging ions. The explanation of the action of the hydrogen ion has already been presented.

Some work of Gorbunov (5) gives a more cogent explanation of the differential fixation of  $\text{NH}_4$  and K in bentonite and other colloids. He found that when a podzolic soil, a chernozem, and bentonite were saturated with  $\text{NH}_4$  and then heated to 100°C. the chernozem and the bentonite lost very large quantities of  $\text{NH}_4$ , whereas the podzolic soil lost scarcely any. The Montalto colloid is podzolic in nature; hence, on heating, no  $\text{NH}_4$  is lost. When the bentonite is heated at 105°C. a very large quantity of the  $\text{NH}_4$  is volatilized as  $\text{NH}_3$ , thus markedly reducing the  $\text{NH}_4$  available for fixation, and consequently greatly reducing the magnitude of fixation itself. Hence, on the basis of Gorbunov's work, Montalto colloid should be expected to fix more  $\text{NH}_4$  than would bentonite. With K, however, no such difference should occur, and, as table 11 shows, this is verified experimentally.

In the cases of K and  $\text{NH}_4$ , an increase in fixation with increase in the amount



of the applied ion is noted. This fits in well with the theory that fixation proceeds through the exchange complex (8)<sup>3</sup>, for with increasing application more of the ion enters the complex. This theory will be elaborated in a later paper.

#### EQUIVALENT VS. WEIGHED QUANTITIES

For comparison, quantities of substances equivalent in exchange capacities must be taken; that is, the samples must be so chosen that the total exchange capacity of one sample equals that of the other. Because the samples of hydrogen bentonite were weighed out on the assumption that the exchange capacity was 0.86 m.e. per gram, when actually the exchange capacity was 0.73 m.e., the results obtained are not strictly comparable. If, however, we assume a linear relationship between fixation at the lower exchange capacity and fixation at the higher exchange capacity, we can extrapolate to determine what the K fixation should have been had the correct weight of sample been used. Actually the sample was too small; by multiplying by the factor 86/73, however, the data are corrected to the point desired.

Comparison of the corrected values for K fixed by the hydrogen bentonite and the K fixed by the Montalto hydrogen colloid is interesting. When equivalent quantities of these materials are taken, fixation of K is equal. This means that it is not so much the weight of sample as the quantity of exchange that is important in fixation, and, even more important (in the case of Montalto hydrogen colloid and hydrogen bentonite at least), equivalent quantities of exchange fix equal amounts of K.

#### FIXATION FROM SOLUTION OF MIXED CATIONS

NH<sub>4</sub> and K have been considered individually. Yet, in actual field practice, they are found side by side in the exchange complex of the soil. When present together, these ions have different exchange properties from those of each alone. Jenny and Ayers (6) have shown this to be true from a nutritional standpoint. Because of agronomic implications it was decided to determine fixations when mixtures of the two ions are added to a system.

To duplicate 2.914-gm. samples of hydrogen bentonite were added 10 ml. of NH<sub>4</sub>Cl (0.1250 *N*) plus 10 ml. of KCl (0.1246 *N*), and 20 ml. of NH<sub>4</sub>Cl plus 20 ml. of KCl respectively. These additions were approximately a total of one symmetry concentration in one case and of two symmetry concentrations in the other. The systems were alternately wetted and dried to bring about fixation. Results are shown in table 12.

The results of the competition are indeed unexpected. Whereas it was borne out in the previous experiments that NH<sub>4</sub> fixation is consistently lower than K (table 10) when each is tried singly, in this case where the two ions are allowed to compete, K shows no such edge. Indeed, at the higher concentration, the NH<sub>4</sub> fixed far exceeds the K fixed. Comparison with table 10 shows that NH<sub>4</sub> fixation is hardly affected by the presence of an equal quantity of K; on the other hand, the presence of NH<sub>4</sub> depresses sharply the amount of K fixed.

Evidently the presence of  $\text{NH}_4$  tends to keep K from entering the exchange complex. Peterson and Jennings (16) pointed out that when bentonite is brought into contact with a mixed salt solution, the bases do not enter the exchange complex in the same ratio as that in which they occur in the solution. Jenny and Ayers (6) showed that  $\text{NH}_4$  does exert a peculiar influence over the exchange properties of K.

K and  $\text{NH}_4$  are taken up in different ratios when the concentrations of the cations are varied. Ayers (1) found this to be true. At a very low concentration, he found that more K than  $\text{NH}_4$  was taken up by the soil. As the concentration increases, however, relatively more  $\text{NH}_4$  is taken up, until at a concentration of 0.1 N the  $\text{NH}_4$  taken up is slightly in excess of the K. It is quite possible that the same thing occurs when the mixture of K and  $\text{NH}_4$  which enters the complex is less than the K, and hence K fixation will exceed that of  $\text{NH}_4$ . When the concentration increases, the relative quantity of  $\text{NH}_4$  which enters the

TABLE 12

*Competition between ammonium and potassium in exchange reactions with H-bentonite*

RELATIVE CONCENTRATION OF ADDED IONS	ION FIXED	
	K	$\text{NH}_4$
	<i>m.e.</i>	<i>m.e.</i>
$\frac{1}{2}$ Symmetry K $\frac{1}{2}$ Symmetry $\text{NH}_4$ } .....	0.11	0.10
1 Symmetry K 1 Symmetry $\text{NH}_4$ } .....	0.06	0.14

complex increases; therefore the relative  $\text{NH}_4$  fixation also increases. If the concentrations are great enough, then  $\text{NH}_4$  fixation can be expected to increase at the expense of K fixation, and ultimately exceed it. The results of table 12 may be explained on this basis.

The effect of previous K fixation on subsequent  $\text{NH}_4$  fixation by hydrogen bentonite was also studied. It was found that when only small amounts of K are used, subsequent  $\text{NH}_4$  fixation is only slightly less than the  $\text{NH}_4$  fixation when no K was fixed previously. If, however, sufficiently large quantities of K are added to the bentonite, so that it fixes almost all the K it can, then little or no  $\text{NH}_4$  can be subsequently fixed. The probable reason for this is that all the "fixing positions" are taken up by K and none are available for  $\text{NH}_4$  ions. Under these conditions,  $\text{NH}_4$  cannot be fixed. This ties in closely with the contention that  $\text{NH}_4$  and K are fixed in like manner.

Previous investigations by Joffe and Levine (8) may now be interpreted to show the converse to the above; that is, fixation of  $\text{NH}_4$  has a depressive effect on subsequent K fixation. When Montalto hydrogen clay is saturated with  $\text{NH}_4$  and then dried there is a marked decrease in the amount of K the clay is able to fix. What probably occurs is that, while drying, the Montalto

clay fixes some of the  $\text{NH}_4$  in the complex, leaving the clay with a lesser ability to fix the K subsequently.

From the series of experiments just reported it is clear that  $\text{NH}_4$  fixation is fully as important as K fixation, and that the two have many similarities. Differences with different materials have been noted, but in general the fixation phenomenon has been demonstrated to be the same for both ions. The interesting influence which  $\text{NH}_4$  exerts on K has been noted and described, as has also been the effect of prior fixation of one of these ions on the subsequent fixation of the other.

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# NUTRIENT CULTURE OF CROPS WITH THE USE OF SYNTHETIC ION-EXCHANGE MATERIALS

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In the winter of 1944 the Army Air Forces undertook to grow vegetable crops by the gravel culture method at overseas bases where no suitable agricultural soil was available. The scarcity of personnel qualified to deal with the technical aspects of preparation, testing, and adjustment of ionic concentrations in nutrient solutions made it desirable to explore the possibility of using a simplified large-scale nutrient culture technique.

The present study was begun with the general objective of approaching, in an artificial culture technique, the relative simplicity of soil management practices used in soils adequately supplied with plant nutrients but requiring the addition of water by periodic irrigations. This was thought possible of realization by the use of sand or gravel culture medium, in which plant nutrients were supplied in an adsorbed form. The following advantages were anticipated: (a) At the beginning of a growing season sufficient quantities of all plant nutrients could be incorporated in the inert substrate to suffice for the production of a crop. This would dispense with the need for preparation, repeated analysis, and replenishment of liquid nutrient solutions. Only the addition of water would be necessary to ensure growth. (b) Elimination of complications in the management of nutrient solutions arising from shifts in pH, depletion of individual nutrients, mutual precipitation of ions, and osmotic pressure variations. (c) Material reduction of losses of plant nutrients from a culture bed through leaching during periods of continuous rainfall. (d) Feasibility of varying the concentration of single nutrient ions without simultaneous variation in the concentration of ions of opposite charge.

Schlenker (10) and Converse, Gammon, and Sayre (4) have successfully grown plants in sand or gravel culture, supplying the nutrient ions in an adsorbed form. The cations were adsorbed on clay colloids (4) or artificial zeolites known under the trade names "Decalso" and "Zeo-Karb-H" (4, 10). The anions were adsorbed on an aniline material named "De-Acidite." In recent years a group of synthetic resins possessing ion-exchange properties, known as "Amberlites" became available. Depending on the method of preparation, Amberlites have either anion- or cation-exchange properties. The Amberlite cation-exchanger is reported to be a phenol-formaldehyde resin in which the hydrogen of the phenolic group is exchangeable for other cations; the anion-exchanger is an

<sup>1</sup> This work was done under contract between the Aero-Medical Laboratory, Air Technical Service Command, and the Division of Plant Nutrition of the University of California. The technical assistance of the personnel of the Nutriculture Detachment, Air Technical Service Command, is acknowledged.

amine-formaldehyde resin (6). The published characteristics of these materials<sup>2</sup> indicated that they should prove to be ion-exchangers of high efficiency and capacity and might serve as suitable carriers of plant nutrients in an adsorbed form. In the present investigation a complete nutrient medium was compounded by combining nutrient anions and cations adsorbed on the two types of Amberlite respectively. Although there was no prior record of an attempt to use Amberlites as sources of all plant nutrients for growing plants without soil, two reports contributed pertinent information on the feasibility of adopting Amberlite ion-exchangers as carriers of plant nutrients. An indirect conclusion that Amberlites might have been presumed not to be toxic for plant growth was drawn from the work of Liebig, Vanselow, and Chapman (9), who found cation- and anion-Amberlites suitable for purification of water used in nutrient solutions. If toxic substances were given off by Amberlites, they would have appeared in the purified water and caused injury to plants. Graham and Albrecht (5) found that nitrate adsorbed on Amberlite anion-exchanger was available for the growth of maize plants and that, unlike soluble nitrogen supplied in the form of calcium nitrate, it was only slightly removed by leaching. While the current investigation was in progress, another report on the properties of Amberlite-nitrate, based on experiments of several years was published by Jenny (8).

#### SCOPE OF INVESTIGATION

The growth of tomato plants through the fruiting stage and the production of market quality fruit in a sand-Amberlite medium were selected as over-all criteria for testing the suitability of the method.

Tomato plants were grown for 5 months in large metal tanks, 25 square feet in surface, filled with sand mixed with the various Amberlite ion-exchangers. The tanks were irrigated daily. Provision was made for including in each successive irrigation the collected drainage from the previous one. Conventional water and sand cultures in parallel tanks served as controls. Following the harvest of the tomato crop the residual nutrient level was tested by growing lettuce in the same tanks.

A more detailed study of plant responses to the various Amberlite combinations was made by growing tomato plants in a series of subirrigated pot cultures. The smaller scale of the installation afforded an opportunity to repeat the large experiments with a greater measure of replication and to submit to a biological test some of the conclusions drawn from the result of chemical analyses. Chemical determinations were made of the inorganic constituents of shoots and fruit from plants grown in several experiments, and periodic analyses were carried out of the solutions percolating through the Amberlite cultures.

In addition to the growth experiments, chemical laboratory studies of the various sand and Amberlite mixtures were made, excluding the plants.

<sup>2</sup> The Amberlites, synthetic resin ion exchange adsorbents. Pamphlet by the Resinous Products and Chemical Co., Philadelphia. 1943.

## EXPERIMENTAL PROCEDURES

*Large-scale tank experiments*

Two experiments were conducted in this series, in which tanks of approximately 460 liters capacity were used. (The tanks were 8 inches deep, 10 feet long, and 2.5 feet wide.) The first experiment constituted the principal effort in the investigation and consisted of growing tomato plants from June 16 to November 21 in sand culture in which plant nutrients were supplied in the form of Amberlite ion-exchangers. The following treatments were included:

Tank 1—sand culture, nutrient solution

Tank 2—water culture, nutrient solution

Tank 3—sand culture, all Amberlite-nutrients, except potassium and nitrate

Tank 4—sand culture, all Amberlite-nutrients

Tanks 1 and 2 represented the controls; all the nutrients were supplied in a standard nutrient solution of the following composition:  $\text{KNO}_3$ , 0.010 *M*;  $\text{Ca}(\text{NO}_3)_2$ , 0.003 *M*;  $\text{MgSO}_4$ , 0.002 *M*;  $\text{NH}_4\text{H}_2\text{PO}_4$ , 0.002 *M*; and A5, a combination of micronutrients Mn, B, Cu, Zn, and Mo (1). Iron was added twice and later thrice weekly at the rate of 0.5 cc. of 0.5 per cent ferrous sulfate solution to a liter of nutrient solution. The management of the sand and water culture tanks was based on the general practices used in this laboratory as described elsewhere (2). To the water culture in tank 2, forced aeration was provided by means of porous carbon tubes.

Tank 4 represented the treatment in which Amberlite ion-exchangers were the sole sources of all plant nutrients, including the micronutrients. Enough of each nutrient was added in an Amberlite form to suffice for the entire growing period, including the requirements of a heavy crop. The nutrient quantities were necessarily estimated but it was felt that data previously obtained in this laboratory (2) on the absorption of nutrients in a 5-month period by tomato plants would form a proper basis for computation. The amounts of potassium, nitrate, calcium, phosphate,<sup>3</sup> and nitrate previously found to be absorbed (2) by twenty tomato plants grown in an aerated nutrient solution culture for 5 months (with an average fruit yield of 21.1 pounds per plant) were mixed in their respective Amberlite form. In addition to these five nutrients, for which absorption data were available, the following Amberlite-nutrients<sup>4</sup> were added: sulfate, iron, manganese, and boron. The amounts used are given in table 1. For sulfate, the same number of milliequivalents were added as for magnesium. The quantities of micronutrients were computed to furnish the following amounts

<sup>3</sup> See footnote †, table 1.

<sup>4</sup> For the sake of brevity, the following nomenclature will henceforth be used: *Amberlites*, a collective term describing the synthetic resins Amberlite IR-100 and Amberlite IR-4, capable of adsorbing or exchanging for cations or anions respectively; *Amberlite-ion*, any ion, either cation or anion, adsorbed on Amberlites; *Amberlite-cation* and *Amberlite-anion* are used to describe the two classes of Amberlite-ions; *Amberlite-nutrient*, an Amberlite-ion in which the ion concerned is a plant nutrient. If reference is made to a specific Amberlite-ion, designations such as *Ca-Amberlite* and *Amberlite-NO<sub>3</sub>* may be encountered.

per plant: iron, 50; manganese, 30; boron, 20 mgm. The Amberlite materials going into a respective tank were mixed together and the mixture was again thoroughly mixed with the sand by shoveling and screening.

As shown in table 1, potassium and nitrate ions required the largest quantities of Amberlites. The suggestion presented itself that the advantages of the ion-exchanger technique would also be realized if these two nutrients were supplied in a solution rather than an Amberlite form. The only modification in technique would consist of substituting a dilute solution of potassium nitrate for water in irrigating the beds. Since both potassium and nitrate are rapidly absorbed ions, no residual accumulations with resultant complications, such as shift in pH, would ensue. A provision was therefore made to test this ex-

TABLE 1  
*Composition of complete Amberlite nutrient medium\**

NUTRIENT ION	TOTAL NUTRIENT ION ADDED	AMBERLITE OF RESPECTIVE ION		
		Capacity	Moisture	Amount added
	<i>m.e.</i>	<i>m.e./dry gm.</i>	<i>per cent</i>	<i>gm.</i>
Ca <sup>++</sup> .....	8,650	1.78	17.2	5,865.2
Mg <sup>++</sup> .....	3,840	1.73	16.7	2,660.5
K <sup>+</sup> .....	14,200	1.46	19.1	12,032.3
Fe <sup>++</sup> .....	34.6	1.71	15.9	24.2
Mn <sup>++</sup> .....	21.4	1.10	13.3	22.5
NO <sub>3</sub> <sup>-</sup> .....	21,270	3.66	8.8	6,387.0
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> .....	972	4.6†	10.6	258.7
SO <sub>4</sub> <sup>-</sup> .....	3,880	5.87	12.3	754.5
H <sub>3</sub> BO <sub>3</sub> .....	31.3	0.5‡	15.1	80.0

\* No deliberate addition of zinc, copper, and molybdenum was made. Reliance was placed on the impurities in the nutrient media.

† The phosphate capacity originally computed by the supplier was 13.68 m.e. per dry gram. This figure was used in determining the amount of Amberlite-phosphate added to the nutrient medium. Subsequent recalculations showed that the actual phosphate capacity of this material, in terms of H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, was only 4.56 m.e. per dry gram.

‡ The figure given for boron is per cent wet weight rather than m.e./dry gram.

perimentally by omitting potassium-Amberlite and Amberlite-nitrate from tank 3. Instead, this bed received daily irrigation with a solution of 0.010 *M* KNO<sub>3</sub>, later reduced to 0.005 *M* KNO<sub>3</sub>. All the other nutrients were furnished as Amberlites in the amounts given in table 1.

The respective Amberlite-ions were prepared by the chemical staff of the Resinous Products and Chemical Company. The Amberlite-cations were made from Amberlite IR-100 by treating different batches with CaCl<sub>2</sub>, MgSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, FeCl<sub>2</sub>, and MnCl<sub>2</sub>, respectively. The Amberlite-anions were prepared by treating Amberlite IR-4 with HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>BO<sub>3</sub>. The moisture content and capacity in milliequivalents per dry gram of each prepared Amberlite-ion, as given in table 1, were determined in the laboratory of the Resinous Products and Chemical Company.

Monterey sand was used to fill tanks 1, 3, and 4. Approximately 630 kgm. of sand was required to fill each tank. The tanks were placed about 2 inches off the ground in such a manner as to give a slope of 1 inch from end to end to facilitate drainage. The water regime in all sand cultures, whether receiving nutrient solution or Amberlites, was the same. It was estimated that the water-holding capacity of a sand bed was around 40 liters. The volumes of liquid used in daily irrigation were less than the water-holding capacity. The same volume of complete nutrient solution, potassium nitrate, or distilled water was applied daily to tanks 1, 3, and 4 respectively. The solution was allowed to stand for about half an hour and then to drain through a hole which was unplugged at the lower end of each tank. The drainage from each tank was collected and measured. In the Amberlite cultures (tanks 3 and 4) the drainage was returned to the respective tank with the next irrigation, supplemented with an additional volume of  $\text{KNO}_3$  solution or water respectively. Thus, a closed system was maintained without loss of leachable material. In tank 1 a closed system was also maintained by returning the leachates, except that, as the salts accumulated in the bed, the leachates were occasionally discarded. In case of the water culture (tank 2), distilled water and chemicals were added as needed.

In order to distribute the risks from insect or disease attack, three varieties were used in each tank: Livingston's Marglobe, Grothen's Red Globe, and Frazier-Gardner<sup>5</sup> (a new variety developed for resistance to spotted wilt). Forty plants were initially planted in each tank and were later reduced to twenty, leaving approximately six of each variety per tank. The seeds were germinated in Monterey sand 4 weeks prior to transplanting into the tanks.

After termination, on November 21, of the tomato experiment described above, a second crop, lettuce, was grown in tanks 1, 3, and 4, to test the residual nutrient level in the Amberlite beds. Tank 1 served as the control. The water-culture bed, represented in the previous experiment by tank 2, was omitted. The stumps of the tomato plants, as well as most of the roots, were removed from the tanks and the beds were fallowed for 1 week. Five-week-old Romaine lettuce plants, previously germinated in sand, were then planted in three rows of twenty plants each per tank; ten additional plants were included in each bed for replacement purposes. As in the previous experiment, chemical analyses were made on the leachates from the respective tanks as well as on samples of plant material.

### *Subirrigated pot experiments*

The plan of the experiment in subirrigated pots is given in table 2. Each treatment was run in triplicate. In setting up the experiment the various cultures were randomized on three greenhouse benches.

The details of the automatic technique, described below, are given in figure 1.

<sup>5</sup> Seed obtained through the courtesy of M. W. Gardner.



TABLE 2

*Plan of experiment in subirrigated pots, and fresh weight of shoots of tomato grown in cultures*  
Average of 9 plants

CULTURE NUMBER	TREATMENT	WEIGHT OF TOMATO SHOOTS
		gm.
1	Distilled water	0.17
2	Nutrient solution	137.4
3	Nutrient solution + 0.03 M NaCl	88.7
4	All Amberlite-nutrients	3.8
5	Same as 4 except 3 × Ca-Amberlite	7.6
6	Same as 4 except 6 × Ca-Amberlite	9.2
7	Same as 4 except 9 × Ca-Amberlite and 2 × Mg-Amberlite	10.0
8	Same as 4 except 3 × concentration of all Amberlite-ions	0.27
9	Same as 4 except 9 × concentration of all Amberlite-ions	0.1
10	Same as 4, plus 0.01 M NaCl	24.8
11	Same as 4, plus 0.03 M NaCl	53.7
12	All Amberlite-nutrients, except K and NO <sub>3</sub> added as 0.01 M KNO <sub>3</sub>	52.1
13	Same as 12 except 3 × concentration of Amberlite-ions	98.2
14	Same as 12 except 9 × concentration of Amberlite-ions	105.6
15	Same as 12, plus 0.01 M NaCl	50.6
16	Same as 12, plus 0.03 M NaCl	39.5

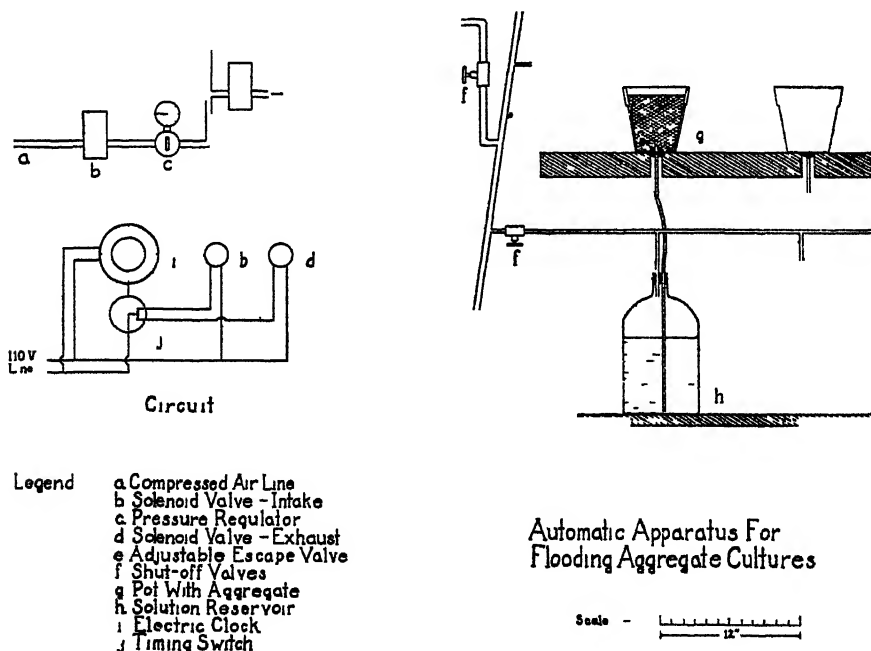


FIG. 1. DIAGRAM OF AUTOMATICALLY SUBIRRIGATED POTS

Standard flower pots, 5 inches in diameter, *g*,<sup>6</sup> were painted with black asphalt inside and with aluminum paint outside. The pots were fitted with a single glass tube and rubber stopper at the bottom. By means of a regulated compressed air system the pots were flooded with solution for 20 minutes of every hour. A total volume of 3 liters of solution was used for each pot. The pots, *g*, placed in proper position on greenhouse tables, were connected through holes in the table with 1-gallon jug reservoirs, *h*, placed on a shelf below. The reservoirs were equipped with a two-holed rubber stopper. One long tube, extending to the bottom of the reservoir, was connected with the pots; a second short tube was connected to the air line. The "lift" for all cultures was standardized, that is, the distance from the top of the sand in the pot to the level of solution in the reservoir, *h*, was adjusted in all cases to 20 inches. A double-circuit electric clock and timing switch, *i* and *j* (General Electric Model 3TS14-AQ), plugged into a standard 110-volt line, opened a solenoid valve, *b*, on a compressed air line, *a*. The compressed air line then passed through a pressure regulator, *c*, into a distribution manifold. The sensitive adjustment of pressure necessary to regulate the height of the flooding solution was obtained by using an adjustable escape valve, *e*, connected to the manifold. This escape valve consisted of an open tube extending 20 inches into a column of water. When the air pressure exceeded that of the hydrostatic pressure of the 20-inch column of water, the excess air escaped into the atmosphere. The pressure regulator, *c*, was adjusted so that there was a moderate stream of air bubbles issuing from this tube after the solution had risen to the top of the aggregate in the pots. At the end of the 20-minute "on" period, the first solenoid valve, *b*, was closed and a second one, *d*, was opened, thus allowing the air under pressure to escape from the manifold and the solution to drain out of the pots. Shut-off valves were placed in the air line at several points. By suitable manipulation of the shut-off valves, *f*, leaks and other difficulties in operation were conveniently located.

The individual Amberlite-ions common to all the Amberlite treatments were mixed together. To a portion of this mixture were then added the K-Amberlite and the Amberlite-NO<sub>3</sub> to provide two "stock" mixtures: one supplying all the nutrient ions and the other supplying all except K and NO<sub>3</sub> in the form of Amberlites. These two stock mixtures were, in turn, modified, as provided by the outline of the experiment (table 2). The Amberlite mixtures for individual pots were thoroughly mixed with dry silica sand by vigorous shaking in a large-mouthed 1-gallon jug. The mixtures of Amberlites and sand were then poured rapidly into the respective pots. Little separation of Amberlite from sand occurred during the growth period.

On February 1, 4-week-old tomato seedlings, variety Rutgers, were planted three to a pot. At 1- or 2-week intervals determinations were made of pH and the specific conductance of the solutions in the reservoirs. Additions of nutrient solution, potassium nitrate, iron, and micronutrients were made to the respective treatments as required.

<sup>6</sup> Letters refer to diagram, figure 1.

### Chemical analyses

Standard methods were used in the analysis of leachates from the various treatments and of the nutrient solutions and in determining the inorganic constituents of plant tissues (2). The fruit and foliage samples were prepared for analysis in the manner used in previous investigations (3).

## RESULTS

### Large-scale tank experiments

*Tomato experiment.* For the first several weeks of growth no untoward symptoms were observed in the young seedlings from the two Amberlite-nutrient combinations used. Plants receiving all nutrients in Amberlite form (tank 4) made less growth than those in tank 3, in which potassium and nitrogen were supplied in the form of 0.010 *M* KNO<sub>3</sub>. Especially noticeable was the reduced growth of foliage in tank 4. Plants grown in tanks 1 and 2, in which conven-

TABLE 3  
*Fresh weight of tomato shoots 3 weeks after being transplanted*  
Average of 7 plants

TANK NUM- BER	TREATMENT	WEIGHT OF SHOOTS		
		Marglobe	Grothen globe	Frazier- Gardner
		gm.	gm.	gm.
1	Sand culture, nutrient solution	25.3	24.6	16.3
2	Water culture, nutrient solution	28.2	42.3	32.6
3	Sand culture, all Amberlite-nutrients, except K and NO <sub>3</sub> added as 0.01 <i>M</i> KNO <sub>3</sub>	17.2	20.6	14.5
4	Sand culture, all Amberlite-nutrients	7.1	13.4	9.3

tional nutrient solutions were used, made more rapid growth than those in either of the two Amberlite treatments. The relative rates of growth of 3-week-old plants are indicated in table 3.

Although the fresh weights of young plants, as shown in table 3, indicated a significantly reduced growth in plants receiving the complete Amberlite-nutrient mixture, no specific deficiency symptoms were apparent. The general conclusion drawn at the time the plants were young was that though plants grown with Amberlite-nutrients did not grow so rapidly as did those in nutrient solutions, there was no indication that Amberlites were unsuited as carriers of plant nutrients in exchangeable form.

Within a few weeks, however, this conclusion was questioned for the "all Amberlite-nutrients" treatment (tank 4). Beginning with the sixth week, distress symptoms began to appear in plants receiving this treatment. Margins of leaves turned brown and became desiccated, tips of leaflets withered away, and a breakdown of petioles with subsequent collapse of leaves was observed (fig. 2). The foliage symptoms in tank 4 were soon followed by a pronounced

blossom drop. Abscission occurred at a point on the pedicel about 1 cm. from the calyx. Such fruit as had set showed blossom-end rot. The general distribution of the symptoms throughout the tank and their absence in adjoining plants grown under different nutrient conditions strongly suggested that the observed injury was caused by some nutrient condition rather than by an extraneous factor such as damage from fumigation, for example. It was especially noteworthy that, unlike plants receiving all their nutrients from Amberlites (tank 4), those grown in tank 3, where Amberlite-nutrients were also used but with the exception of K and  $\text{NO}_3$ , were free from any injury. The foliage symptoms on plants in tank 4 resembled those of calcium deficiency. Although this conclusion seemed at first untenable, since the plants in tank 3 received the same amount of calcium in the form of Ca-Amberlite and

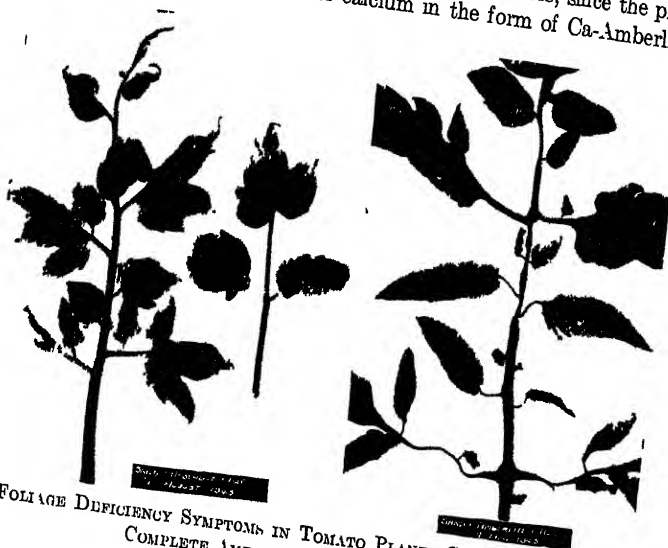


FIG. 2. FOLIAGE DEFICIENCY SYMPTOMS IN TOMATO PLANTS GROWN FOR 6 WEEKS IN A COMPLETE AMBERLITE MEDIUM (TANK 4)

no other, it was decided to add a solution of calcium to tank 4 on the supposition that, unlike tank 3, the Ca-Amberlite in tank 4 failed to yield available calcium for plant needs. Accordingly, on August 9, the drainage from tank 4 was discarded and 30 liters of solution, containing 133 p.p.m. of Ca as  $\text{CaSO}_4$ , was applied. On subsequent days the drainage was returned to the tank, supplemented with varying volumes of calcium sulfate solution of the same concentration. Since the possibility existed that the other divalent cation, magnesium, might also be unavailable in tank 4, additions of  $\text{MgSO}_4$  were begun a week after the first application of  $\text{CaSO}_4$ . The total volume of liquid returned to the tank was fortified each day with 45 p.p.m. Mg. The daily applications of calcium and magnesium were continued for 9 weeks. The additions of calcium and magnesium were then discontinued, and applications of only distilled water were resumed during the remaining 7 weeks of the growth period. It

was assumed that as a result of the previous treatment, enough calcium and magnesium had been accumulated in the beds to suffice for the duration of the experiment.

A marked and favorable response was observed soon after the additions of calcium and magnesium were made. Normal vegetative growth was resumed by the plants, the new leaves being free from deficiency symptoms. Abscission of blossoms ceased and normal fruit setting was in evidence on newly grown shoots. Figure 3 shows the general appearance of plants in the all-Amberlite



FIG 3 TOMATO PLANTS 19 WEEKS AFTER BEING TRANSPLANTED (11 WEEKS AFTER Ca AND Mg APPLICATIONS WERE BEGUN)

Left to right. tank 1—sand culture, nutrient solution; tank 2—water culture, nutrient solution, tank 3—sand culture, all Amberlite-nutrients, except potassium and nitrate; tank 4—sand culture, all Amberlite-nutrients.

treatment about 11 weeks after the calcium and magnesium applications were begun (19 weeks from the time of transplanting).

Plants grown with conventional nutrient solutions, whether in sand or in water culture, made excellent vegetative growth and were fruitful. The differences observed among the three varieties used are not particularly germane to the main purpose of this investigation and accordingly have been noted only incidentally (table 4). Plants in tank 3, receiving Amberlite-nutrients except for potassium and nitrogen, also made excellent growth and showed sustained fruit production during the major part of the growing period. During the

twentieth week, however, slight symptoms, somewhat indicative of phosphate deficiency, were observed. Still, there was no marked decrease in the rate of growth and fruit production.

The yield of fruit from the several treatments is given by variety in table 4. Because of the early nutritional disturbance, fruit from the lower clusters failed to develop in tank 4, and the reported yields for that treatment represent a harvest period only about half as long as that for the other treatments. For comparable period of harvest the yields from tank 4 might be regarded as of the same general order of magnitude as those from other treatments. This can be taken as another line of evidence in support of the complete recovery, following the application of calcium and magnesium, of plants in tank 4 in which all the nutrients were supplied as Amberlites.

TABLE 4  
*Average fruit yield\* of tomato plants grown from June to November*  
Averages of 7 plants

TANK NUM- BER	TREATMENT	FRUIT YIELD		
		Marglobe	Grothen globe	Frazier- Gardner
		<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>
1	Sand culture, nutrient solution	12.9	10.2	8.1
2	Water culture, nutrient solution	9.7	10.3	6.6
3	Sand culture, all Amberlite-nutrients, except K and NO <sub>3</sub> added as 0.01 M KNO <sub>3</sub>	7.8	8.4	6.7
4	Sand culture, all Amberlite-nutrients†	4.0	3.7	6.4

\* These figures include sound green fruit from plants at time experiment was terminated. The proportion of green fruit in the figures cited varied from about 10 per cent in tank 3 to about 30 per cent in tank 4.

† Because of early growth disturbances (see discussion in text), the harvest of fruit from this treatment began in the week ending October 13, 7 weeks after that of the other treatments.

The results of this experiment indicated that when all plant nutrients were furnished in the form of Amberlite ion-exchangers, tomato plants were unable to absorb enough calcium and possibly magnesium. The same amounts of calcium- and magnesium-Amberlite were adequate, however, as sources of these nutrients when, as in tank 3, only a partial Amberlite-nutrient medium was provided: specifically, when a KNO<sub>3</sub> solution was used as the source of potassium and nitrogen. As pointed out earlier, the nutrient technique, as represented by the treatment in tank 3, may be regarded as a successful attainment of most if not all of the objectives. Nevertheless, the question of calcium availability, as exemplified by the results from tank 4, made it advisable to examine more intensively the properties of Amberlites as carriers of plant nutrients. What follows deals principally with the additional investigations carried out in this direction.

*Lettuce experiment.* In order to test fully the residual nutrient status of the

Amberlite beds, the lettuce planted in tanks 3 and 4 received the same nutrient treatment as was given to the preceding crop of tomatoes at the time the experiment was terminated. Thus, tank 3 was irrigated with 0.005 *M* KNO<sub>3</sub>, and distilled water only was given to tank 4. The leachates from the respective tanks were brought up each day to a volume of 15 liters and returned to the tanks. Tank 1, receiving a complete nutrient solution, was used as a control. Within a few days after planting, indications were that the nutrient level in tank 4 (complete Amberlite-nutrient mixture) was inadequate for ready establishment of the seedlings. Eight plants had to be replanted in this tank but none in tank 3 (Amberlite-nutrients plus KNO<sub>3</sub>). In another week or so, however, plants in tank 4 seemed to be well established, presumably following the development of a larger root system, which was capable of drawing on a larger volume of the nutrient medium. The plants were uniform and apparently healthy, although they attained only about one third the size of the controls in tank 1.

The plants in tank 3 established themselves in the bed without difficulty, probably as a consequence of the daily irrigations with the potassium nitrate solution. During the second and third week, however, growth became visibly reduced and irregular, with wide variations in size among the plants. A partial harvest about 6 weeks after planting disclosed that the average fresh weight of plants from tank 4 was 28 per cent of that of the controls in tank 1, whereas the average weight for tank 3 was only 18 per cent (average of 30 plants).

No specific deficiency symptoms were observed at the time of the partial harvest. Ten days later, however, a few of the plants in tank 3 began to show definite calcium deficiency. The innermost leaves had darkened edges and showed symptoms of complete breakdown of the growing point. The calcium-deficiency symptoms were clear-cut only in the larger plants. Some of the smaller plants had been severely stunted and had dead growing points—a symptom usually associated with calcium deficiency. The plants in tank 4 were uniform in size and showed no deficiency symptoms but a general reduction in growth as compared with the controls in tank 1. The plants in tank 4 were distinctly better, however, than those in tank 3.

It will be recalled that in the preceding tomato experiment calcium-deficiency symptoms appeared in tank 4 rather than in tank 3. The apparent reversal in the present experiment is consistent, however, with the fact that no calcium was added to tank 3, except for the initial addition of Ca-Amberlite, whereas irrigations with CaSO<sub>4</sub> were made in tank 4. The results with lettuce led to the conclusion that the calcium supply in tank 3 became exhausted, whereas the CaSO<sub>4</sub> additions to tank 4 left a residual supply of available calcium. The latter is also indicated by the fact that toward the end of the preceding tomato experiment additions of CaSO<sub>4</sub> to tank 4 were eliminated without any impairment in growth and fruit production.

#### *Subirrigated pot experiments*

The scope of these growth tests is obtained from table 2, which gives the average fresh weights of plants grown in the different cultures. A set of pots

irrigated with distilled water (treatment 1) afforded a check on the possible impurities of nutrient significance carried in the sand; the nutrient solution treatments (Nos. 2 and 3) served as the controls with which the various Amberlite treatments were compared.

The basic pattern of these experiments consisted in reproducing the "all Amberlite nutrients" and the "all Amberlite-nutrients except  $K^+$  and  $NO_3^-$ " treatments (tanks 4 and 3) of the large-scale tomato experiment, with a number of variants intended to throw some light on the nature of the results previously obtained. The "all Amberlite-nutrients" and the "all Amberlite-nutrients except K and  $NO_3$ " treatments in the former experiment were represented in the subirrigated pot series by treatments 4 and 12 respectively (table 2). The same proportions of sand to Amberlites as were used in the large-scale experiment were adopted for the corresponding treatments in the pot cultures. All variations in the concentration of Amberlites in the treatments were multiples of the original concentrations used in treatments 4 and 12.

The following modifications of these two basic Amberlite treatments were included: increased concentrations of Ca- and Mg-Amberlites, increased concentrations of all Amberlite-nutrients, and additions of NaCl. The increased calcium- and Mg-Amberlite supply was suggested by the apparent nonavailability of calcium and possibly magnesium in the all-Amberlite treatment. It was reasoned that by increasing the concentration of these Amberlite-ions in the nutrient medium an opportunity would be provided for a greater number of contacts between root surfaces and Ca- and Mg-Amberlite particles. The corresponding increase in the concentration of all Amberlite-nutrients in another set of cultures permitted testing the effect of increased calcium and magnesium supply when the relative proportions of all Amberlite-ions were maintained as in the basic treatments. Moreover, by increasing the total concentration of Amberlites a test was made of the possible toxicity effects of relatively large amounts of Amberlite-nutrients initially incorporated in the cultures. The sodium chloride modifications were introduced following the discovery that the sand used in the large-scale tank experiments was contaminated with salt.

Within a few weeks marked differences in growth were apparent among the different treatments. Special interest was attached to the comparison of treatments 12 and 4 (table 2) which paralleled those in tanks 3 and 4 of the previous experiment. At the beginning of the fourth week a marked reduction in growth was evident in culture 4, receiving all nutrients as Amberlites. No such reduction was observed in treatment 12, in which the K- and  $NO_3$ -Amberlites were omitted and 0.01 M  $KNO_3$  was used. The superiority of treatment 12 over 4, as shown in table 2, is thus in accord with the growth responses obtained in the previous large-scale experiment, in which lack of available calcium checked growth in the all-Amberlite treatment (tank 4). It will be noted that, in the present experiment, increasing the Ca-Amberlite in the all-Amberlite series threefold, sixfold, or even ninefold gave only slight increases in growth and by no means induced growth comparable to that in the treatment 12 series (cf. treatments 6 and 7, table 2).



Neither was the threefold and ninefold increase of all the Amberlite nutrients (treatments 8 and 9) followed by improved growth. On the contrary, these were the least favorable treatments within the "all Amberlite-nutrients" series. Marked stunting and severe injury associated with necrosis of new leaves were observed in these treatments early in the growing season. In total growth these plants were about on a par with those in treatment 1 (no Amberlites, distilled water only). In contrast, multiplication of the Amberlite concentration in the treatment 12 series by 3 and by 9 was accompanied by large and favorable responses in growth (treatments 13 and 14, table 2). Thus, whatever the cause of the injury from increasing the Amberlite-nutrients, it was confined to the series in which K-Amberlite and Amberlite- $\text{NO}_3$  were present in combination with other Amberlite-nutrients.

Of special interest were the results from the additions of NaCl to the all-Amberlite combination (treatments 10 and 11). Among those included in the present series, these were the only treatments that gave large and favorable improvement in growth in cultures supplied with the complete Amberlite-nutrient combination. The improvement was more marked from adding the more concentrated NaCl solution. No such improvement, however, following the addition of NaCl was observed in the "all-Amberlite, except K and  $\text{NO}_3$ " cultures (treatments 15 and 16). As a matter of fact, in this series the higher NaCl concentration (treatment 16, table 2) was associated with a reduction in growth.

### *Results of chemical analyses*

*Analyses of leachates.* At the beginning of these experiments samples of the leachates from the large-scale tank experiments were analyzed several times a week for potassium and nitrate. Later, these periodic analyses were extended to include all the principal nutrient ions as well as pH determinations. The results of these analyses are summarized in table 5. For the sake of brevity, only the data for the Amberlite treatments are included.

Contrary to expectations based on the results of Graham and Albrecht (5), the first analyses of the leachate from tank 4 disclosed a relatively high solubility of nitrate from Amberlite-nitrate. Unlike those of the previous workers, the present experiments included combinations of both cation- and anion-Amberlites and the question arises whether the solubility of nitrate is explained by some interaction between the different Amberlite-ions. Another factor which might have played an important part in accounting for the amounts of nitrate brought into solution was a NaCl contamination in the sand. The initial concentration of NaCl is not known, but the evidence at hand indicates that important quantities of chloride were present and they might perhaps have displaced nitrate ions from the Amberlites.

The first calcium and magnesium analyses disclosed the much higher concentration of these ions in the leachate from tank 3 than in that from tank 4. In tank 4, after the additions of calcium and magnesium had been continued for a number of weeks, the concentrations of these ions in the leachate increased,

reaching their peak in October, when the additions were discontinued. In tank 3, to which no additions of Ca and Mg were made during the growing season, the initially high concentration of these ions in the leachate decreased, no doubt as a result of absorption by the plants, until it approximated the levels

TABLE 5

*Average analyses of leachates from sand cultures supplied with Amberlite-nutrients (tomato experiment)\**

WEEK ENDING	K <sup>+</sup>		Ca <sup>++</sup>		Mg <sup>++</sup>		PO <sub>4</sub> <sup>=</sup>		NO <sub>3</sub> <sup>-</sup>		pH	
	Tank 3†	Tank 4‡	Tank 3	Tank 4	Tank 3	Tank 4	Tank 3	Tank 4	Tank 3	Tank 4	Tank 3	Tank 4
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.		
July												
14									371	2200		
21									428	2630		
28	184	723							504	1105	6.62	5.74
Aug.												
4	172	553					28	16	242	903	6.80	6.02
11	240	432	67	6	50	1	15	11		780	7.15	6.35
18			60	5	29	1	17	11	387	618	6.98	6.04
25			58	3	29	1	13	14	421	540	7.13	6.23
Sept.												
1			69	4	22	1	17	16	416	508	7.22	6.29
8	272	367	33	3	20	1	6	11	468	709	7.38	6.23
15	248	393	30	6	18	3	6	9	487	755	6.96	6.25
22	187	477	18	9	8	4	4	9	417	799	7.11	6.27
29	179	355	15	10	7	5	5	7	459	790	7.26	6.35
Oct.												
6	187	505	15	31	8	27	4	13	452	966	7.15	6.15
13	163	552	9	28	6	26	3	13	437	1107	7.32	6.45
20	177	433	6	16	4	12	2	10	485	940	7.40	6.46
27	189	283	8	8	5	7	2	6	453	810	7.42	6.75
Nov.												
3	195	278	7	6	4	4	2	7	460	659	7.20	6.40
10	203	228	7	3	2	2	2	4	462	517	7.00	6.44
17	228	200	8	2	4	1	2	5	531	427	7.15	6.39
24	217	138	6	2	4	1	2	4	507	338	6.96	6.26

\* Intermittent additional analyses gave the following results for tank 3 and Tank 4 respectively: *chlorides*—24 November, 7 and 36 p.p.m.; 20 October, 18 and 163 p.p.m.; 4 August, 728 and 191 p.p.m.; *sulfates*—27 October, 241 and 113 p.p.m.; 24 November, 188 and 119 p.p.m.

† Tank 3—all Amberlite-nutrients, except K and NO<sub>3</sub>.

‡ Tank 4—all Amberlite-nutrients.

which, in tank 4, gave rise to deficiency symptoms in August. This is further shown in table 6. The results of the previously discussed lettuce experiment, in which calcium-deficiency symptoms did appear in tank 3, are of interest in this connection.

As shown in tables 5 and 6, after the additions of calcium and magnesium

to tank 4 had ceased, the concentrations of these ions in the leachate dropped to levels lower than those in tank 3. Yet, unlike the lettuce plants grown in tank 3, those in tank 4 showed no evidence of calcium deficiency. Nor was there any indication of lack of calcium in the last part of the growth period of the tomato plants grown in tank 4, prior to the planting of lettuce. This suggests that the same low levels of ionic concentration, which were indicative of calcium deficiency when Ca-Amberlite was the only source of calcium, were no longer a reliable guide when calcium salts were introduced into the bed. It is possible that the daily applications of calcium and magnesium resulted in localized precipitation of these as sulfates and phosphates, which supplied some available calcium and magnesium at the root surfaces without being reflected in the analyses of the leachates.

TABLE 6

*Average analyses of leachates from sand cultures supplied with Amberlite-nutrients (lettuce experiment)\**

WEEK ENDING	K <sup>+</sup>		Ca <sup>++</sup>		Mg <sup>++</sup>		PO <sub>4</sub> <sup>=</sup>		NO <sub>3</sub> <sup>-</sup>		pH	
	Tank 3†	Tank 4‡	Tank 3	Tank 4	Tank 3	Tank 4	Tank 3	Tank 4	Tank 3	Tank 4	Tank 3	Tank 4
Dec.	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>		
4	196	98	8.5	2.5	5.6	.2	2.3	2.4	497	210	7.3	6.5
10	261	118	8.5	2.3	5.6	1.1	1.9	2.7	519	250	7.0	6.2
17	254	98	8.9	2.2	4.7	.5	2.0	2.2	546	231	7.0	6.2
26	262	92	8.3	2.5	4.6	0.1	2.0	3.2	510	270		
Jan.												
2	221	224	7.5	7.0	1.1	2.6	1.6	1.5	525	520	7.0	7.0
9	262	92	8.0	2.8	6.1	3.0	2.1	3.6	581	248	7.0	6.3
16	277	59	11.0	2.0	5.5	2.4	1.8	3.5	232	232	7.2	6.3
23	254	80	7.5	2.0	4.2	0.	1.7	3.1	577	261	7.0	6.3

\* On 23 January the following supplementary determinations were made for tank 3 and tank 4 respectively: chlorides, 17.7 and 50.7 p.p.m.; sulfates, 163 and 14.1 p.p.m.

† Tank 3—all Amberlite-nutrients, except K and NO<sub>3</sub>.

‡ Tank 4—all Amberlite-nutrients.

The previously discussed growth data and the analyses of the leachates suggest that calcium and magnesium were relatively unavailable to plant roots when an "all Amberlite-nutrients" combination was used. This conclusion is further strengthened by the following results.

*Analyses of plant tissues.* Table 7 gives the results of analysis of 3-week-old tomato plants grown in the first large-scale experiment. It will be recalled that beyond a general reduction in growth, the plants at that stage exhibited no deficiency symptoms. Nevertheless, the analytical results in table 7 demonstrate a marked reduction in calcium and magnesium content in the vegetative tissues of plants given all nutrients as Amberlites (tank 4). The high potassium content of the low-calcium tissues is in accord with known facts of interionic relations, as observed in many investigations with soils and nutrient cultures.

The calcium content of plants in tank 3, supplied with the same amount of Ca-Amberlite but given 0.010 *M* KNO<sub>3</sub>, is comparable with that of plants in tank 1, grown with a standard nutrient solution. There is no evidence of reduction, but rather an increase, in the calcium content.

A reversal of this picture is seen in table 8. This material was collected for analysis 17 weeks later. Following the applications of calcium and magnesium to tank 4, normal growth was resumed, and this is reflected in the high calcium

TABLE 7

*Inorganic composition of leaves and stems of 3-week-old tomato plants, variety Marglobe*  
Per cent dry weight

TANK NUMBER	TREATMENT	LEAF BLADES					STEMS				
		K	Ca	Mg	PO <sub>4</sub>	N	K	Ca	Mg	PO <sub>4</sub>	N
1	Sand culture, nutrient solution	4.0	2.0	1.3	2.7	5.7	9.7	1.0	1.1	2.6	4.4
3	Sand culture, all Amberlite-nutrients, except K and NO <sub>3</sub> added as 0.01 <i>M</i> KNO <sub>3</sub>	3.9	2.5	1.3	2.2	5.5	9.6	1.3	1.1	2.1	4.2
4	Sand culture, all Amberlite-nutrients	7.3	0.6	0.5	1.9	5.4	15.4	0.3	0.4	1.3	3.9

TABLE 8

*Inorganic composition of leaves and stems of 20-week-old tomato plants, variety Marglobe*  
Per cent dry weight

TANK NUMBER	TREATMENT	LEAF BLADES					STEMS				
		K	Ca	Mg	PO <sub>4</sub>	N	K	Ca	Mg	PO <sub>4</sub>	N
1	Sand culture, nutrient solution	4.5	1.3	0.6	2.6	4.9	8.8	1.2	0.5	3.0	3.1
3	Sand culture, all Amberlite-nutrients, except K and NO <sub>3</sub> added as 0.01 <i>M</i> KNO <sub>3</sub>	4.7	0.5	0.4	0.7	4.1	9.2	0.7	0.4	0.3	2.2
4	Sand culture, all Amberlite-nutrients	3.8	1.4	0.4	0.7	4.2	6.7	1.5	0.5	0.6	2.0

content of the foliage. In tank 3, however, as shown by the analyses of leachates in table 5, the calcium level was reduced. Although no distinct calcium-deficiency symptoms were in evidence, the vegetative tissues showed a decrease in calcium content. This finding is in harmony with the results of the previously discussed second-crop lettuce experiment, in which calcium deficiency appeared in tank 3. The analyses of the lettuce plants as shown in table 9 are also consistent with this interpretation. The calcium content of plants from both tanks 3 and 4 was less than that of plants grown in tank 1 (nutrient

solution). But as between tanks 3 and 4, the plants in the former had a lower calcium content later in the season.

Attention is directed to the lower phosphate content of plants grown in the Amberlite treatments as compared with those grown with nutrient solutions (tables 8, 9, and 10). This is probably related to the low total amount of Amberlite-phosphate used, as a result of an error in computation (see footnote †, table 1). The amount of Amberlite-phosphate actually incorporated in the beds was only about a third of that indicated by the data from other sources which served as a basis for computing the amounts of all the other Amberlite-

TABLE 9  
*Inorganic composition of 6-week-old Romaine lettuce plants*  
Per cent dry weight

TANK NUMBER	TREATMENT	K	Ca	Mg	PO <sub>4</sub>	N	SO <sub>4</sub>
1	Sand culture, nutrient solution	8.8	1.0	0.6	2.6	0.2	1.0
3	Sand culture, all Amberlite-nutrients, except K and NO <sub>3</sub> added as 0.01 M KNO <sub>3</sub>	6.3	0.4	0.3	1.0	0.3	1.1
4	Sand culture, all Amberlite-nutrients	7.0	0.7	0.4	0.9	0.4	1.0

TABLE 10  
*Inorganic composition of tomato fruit*  
Per cent dry weight

TANK NUMBER	TREATMENT	VARIETY	K	Ca	Mg	PO <sub>4</sub>	N
1	Sand culture, nutrient solution	Frazier-Gardner	5.64	.053	.33	2.72	3.40
		Grothen Globe	4.50	.063	.20	1.81	2.48
		Marglobe	4.32	.076	.23	2.00	2.40
4	Sand culture, all Amberlite-nutrients	Frazier-Gardner	5.07	.043	.27	1.09	2.80
		Grothen Globe	4.18	.077	.18	0.70	2.18
		Marglobe	3.98	.072	.20	0.83	2.17

nutrients (2). The reduction in the phosphate content of plant tissue was very marked in the latter part of the growing season; the differences in the phosphate content of young plants were less pronounced (table 7).

The inorganic composition of fruit grown in an Amberlite medium is given in table 10. A comparison was made between fruit grown in tank 4 and that grown in tank 1. Except for phosphate, the data indicate no wide variation in the inorganic composition of fruit grown in the two mediums. This is in general accord with other findings (3) that the mineral composition of the fruit, as contrasted with that of the vegetative parts, is not subject to wide fluctuations. A distinct mineral deficiency would make normal fruit development impossible.

*Laboratory leachings of Amberlite mixtures.* The unavailability of calcium and magnesium in the all-Amberlite treatment and the apparent effect of  $\text{KNO}_3$  in rendering these bivalent ions available suggested the desirability of checking these effects under more rigorous laboratory conditions. It was decided to simulate in the laboratory the chemical systems used in the growth experiments in the greenhouse, omitting, however, the plants. One kilogram of dried silica sand was thoroughly mixed with a mixture of "all Amberlite-nutrients" in the same proportions as given in table 1 for tank 4. The mixture was placed in a percolation column equipped with a small wad of glass wool in the bottom. The column was then leached with 1 liter of water and allowed to drain freely. The leachate was collected and poured again through the column at regular intervals. This operation was repeated until a total of 35 recirculations or

TABLE 11  
*Results of chemical analyses of leachates and extracts of Amberlite mixtures*

	SPECIFIC CONDUCTANCE $\times 10$	pH	$\text{K}^+$	$\text{Ca}^{++}$	$\text{Mg}^{++}$	$\text{NO}_3^-$	$\text{H}_2\text{PO}_4^{--}$
	<i>mhos</i>		<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
1. Leachate from 1000 gm. of sand mixed with all Amberlite-nutrients. Washed with 1,000 cc. $\text{H}_2\text{O}$ .....	153	4.03	5.39	0.07	0.0	3.82	0.11
2. Leachate from 1000 gm. of sand, mixed with all Amberlite-nutrients, except K and $\text{NO}_3$ . Washed with 1000 cc. of 0.01 $M$ $\text{KNO}_3$ .....	275	4.28	6.88	2.99	1.76	4.83	.85
3. Extract of a mixture of all Amberlite-nutrients, with 1000 cc. $\text{H}_2\text{O}$ .....	82.4	3.60	2.10	0.04	0.0	1.63	0.05
4. Extract of a mixture of all Amberlite-nutrients, except K and $\text{NO}_3$ , with 1000 cc. of 0.01 $M$ $\text{KNO}_3$ .....	306	3.30	7.24	1.38	1.04	6.96	1.13

\* Computed by the following formula:  $\frac{\text{p.p.m. PO}_4^{--}}{95} = \text{m.e. H}_2\text{PO}_4^{--} \text{ per liter.}$

cycles was attained. After the last cycle, samples from the leachate were taken for analysis. A similar technique was used in obtaining leachate samples for analysis from the "all Amberlite-nutrients except K and  $\text{NO}_3$ " treatment. This column was leached with 1000 cc. of 0.010  $M$   $\text{KNO}_3$ .

As a further check on the nature of ionic solubility in Amberlites, extracts of the two mixtures of Amberlites were made by dispensing with sand altogether and extracting the materials with 1000 cc. of water and with 1000 cc. of 0.010  $M$   $\text{KNO}_3$  respectively. The requisite amounts of Amberlites were mixed with either the water or the  $\text{KNO}_3$  in a bottle, and the bottle was stirred in a shaking machine for 52 hours—the time elapsed in completing the leachings of the sand series. Each treatment was replicated four times. The results, as given in table 11, are averages of four analyses, which showed close agreement.

The data in table 11 confirm the results obtained in the greenhouse experi-

ments. The concentrations of calcium and magnesium were very low in both the leachate and the extract from the "all Amberlite-nutrients" combination. When K- and Amberlite- $\text{NO}_3$  were omitted, however, and a dilute solution of  $\text{KNO}_3$  was used, appreciable amounts of Ca and Mg were found in solution. Another interesting fact indicated by table 11 is the lower concentration of phosphate in the leachate and the extract from the "all Amberlite-nutrients" mixture, than in the  $\text{KNO}_3$ -treated combination.

### ✓ DISCUSSION

The results of this investigation indicated that, in terms of the objective sought, an affirmative answer could be given to the question whether Amberlite ion-exchangers can serve as sources of plant nutrients and thereby simplify the present technique of growing plants in an artificial medium without soil. It was shown, however, that the Amberlite technique most suited for growing plants was not the obvious one anticipated at the start, that is, the one in which all the nutrient ions are supplied by Amberlite cation- or anion-exchangers. From this combination, calcium and magnesium were unavailable for plant growth. When, however,  $\text{KNO}_3$  was used, no calcium- or magnesium-deficiency symptoms were observed. The use of  $\text{KNO}_3$  in conjunction with Amberlite-nutrients accomplished most of the principal objectives sought in the new technique. The substitution of  $\text{KNO}_3$  for K-Amberlite and Amberlite- $\text{NO}_3$  also resulted in great economy of materials (see table 1).

The nonavailability of calcium in the "all Amberlite-nutrients" treatment (tank 4), but its availability in the "all Amberlite-nutrients except K and  $\text{NO}_3$ " treatment (tank 3) is not explicable by the present data. One possible hypothesis was that in tank 3 the daily irrigations with  $\text{KNO}_3$  resulted in the replacement of calcium from Ca-Amberlite by the potassium of the  $\text{KNO}_3$  solution. This explanation, however, is not supported by the analyses of leachates from tank 4 (table 5) which indicated large amounts of potassium and nitrate in solution. The full explanation of these results must await further investigation.

From the published properties of Amberlites there was no reason to expect that one Amberlite-ion affected the properties of another, when a mixture of Amberlite-cations and Amberlite-anions, such as used in this investigation, was prepared. But the evidence here presented (table 5) indicates appreciable solubility of adsorbed ions, especially potassium and nitrate, when an Amberlite nutrient mixture was prepared. •

The data presented do not bear directly on the nature of mechanism by which ions adsorbed on the Amberlites were taken up by the roots. The analyses of leachates (table 5) indicate that for ions like potassium and nitrate the amounts dissolved were comparable to those usually included in nutrient solutions. For others, like calcium in the leachate from tank 3, though the concentration is lower than that in most nutrient solutions, there is no reason to believe that it would be necessarily inadequate, if it is assumed that an equilibrium condition obtained and that absorption by plants resulted in additional amounts going into solution. The technique used in this investigation was not designed to

distinguish between absorption from a liquid phase and absorption through "contact exchange" (7) between roots and solid Amberlite particles. All that can be said is that the data do not require the invoking of a "contact-exchange" mechanism to explain the results obtained.

The purpose of this investigation was to gain basic information about the suitability of Amberlite ion-exchangers as a means of simplifying the gravel culture technique for soilless crop production. At the time the investigation was begun, the successful accomplishment of the primary mission rather than economic considerations of cost was the dominant thought. The relative availability and expense of various materials will, of course, receive careful scrutiny under peacetime conditions. The results obtained to date seem to justify further research into the various aspects of the new technique.

#### SUMMARY

An investigation was conducted to determine the feasibility of growing crop plants in sand culture to which plant nutrients were supplied, not in a nutrient solution, but as adsorbed cations and anions on synthetic resins, known as Amberlites.

Tomatoes and lettuce were used as indicator crops. They were grown in surface-irrigated large production-scale beds as well as in subirrigated small cultures.

Chemical analyses were made of leachates from the various cultures and of leaves, stems, and fruits of plants grown under the different experimental conditions.

Two principal nutrient combinations were investigated: (a) one in which all the nutrient ions were furnished in an adsorbed form on Amberlites and (b) another in which potassium and nitrogen were supplied by daily irrigations of a dilute  $\text{KNO}_3$  solution but all the other nutrients were furnished as in (a).

In the (a) treatment calcium and magnesium were found unavailable for plant growth. Good growth and fruiting were obtained in (b).

A discussion is presented of the possible advantages and conditions under which the adsorbed-nutrient technique may find application in crop production without soil.

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## COMMENTS ON THE BASIS OF "CONTACT EFFECT"

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The contact-exchange theory of Jenny and Overstreet† postulates a direct transfer of adsorbed cations between plant roots and clay particles. This phenomenon would take place in all typical soils.

More recently Jenny‡ has postulated a second type of contact relationship between plant roots and solid particles. In the case of electropositive particles coming in contact with the predominantly electronegative root surface there may be unfavorable contact effects. No mechanistic explanation of this adverse contact effect has been developed, but Jenny points out that the intermingling of the two oppositely charged electric double layers may cause the disturbance.

At a time when all plant nutrition problems can apparently be explained in terms of the relations of plant roots to the soil solution, it is difficult to accept any other general theories. However, we have both favorable and adverse contact effects now postulated on the solid basis of colloidal behavior.

Both of these phenomena would possibly be involved in the foregoing investigation reported by Arnon and Grossenbacher.

In this investigation apparent calcium and magnesium deficiency occurred. The culture medium was complicated by the presence of all of the essential ions as well as both cation- and anion-absorbing materials. The various interactions may indeed be complicated. No effort will be made here to discuss every phase of the systems used or to show why the results obtained appeared to be explained by the hypothesis that calcium and magnesium were unavailable.

Before this could be done more will have to be learned about the nature of the postulated adverse contact effect. Other factors to be considered would be: the number of contacts per unit area, the percentage of root area dominated by such contacts, and the influence of the magnitude of the charge on electropositive particles or of the difference in charge between the root surface and the colloidal particle in contact with it.

Let us consider three general points:

1. Adverse plant responses appeared earlier and were more severe when higher concentrations of Amberlite-nutrient were used. Toxicity of Amberlite itself seems to be ruled out because the addition of a dilute salt solution allowed good plant growth. Therefore increasing the number of contacts between plant roots and Amberlite seems to have an adverse effect.

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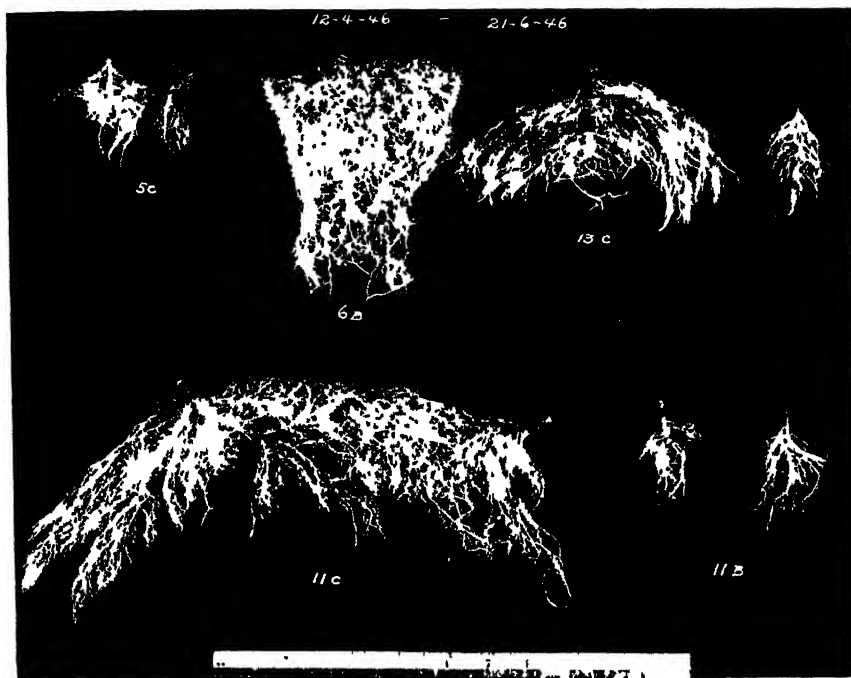
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2. The addition of electrolytes ( $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{KNO}_3$ ,  $\text{NaCl}$ ) improved plant growth. Not only do these additions increase the availability of calcium and magnesium but they also lower the magnitude of the electric charge on colloidal particles. It is probable that even with the same number of contacts the adverse effects would be reduced if the magnitude of the charge was reduced.

3. Additional evidence based on the distribution and development of root systems.

In an additional series of tests, made by the writer, in the previously described automatically irrigated pots the variation in plant response was extremely high. In triplicate



TYPICAL EXAMPLES OF ROOT SYSTEMS DEVELOPED IN AUTOMATICALLY IRRIGATED POTS

5C. Typical small root system in adverse Amberlite culture.

6B. Typical root mass developed in the same Amberlite mixture with the addition of 0.03M  $\text{NaCl}$ .

13C. Root systems from two plants in a single pot showing the heavy shell of roots developed by one of the plants.

11C. A heavy shell of roots (opened and flattened) developed by two plants in the same treatment where two other plants, 11B, in another pot showed typically dwarfed root systems. Note several roots on the extreme right of 11B which had reached the wall of the pot and were beginning to show improved growth.

pots the yield from single pots varied as much as from 1 to 10 in five of the total sixteen treatments. The variation between single plants within the same pot was often even greater. Quite obviously there was some factor in the environment of these plants that was completely out of control.

At the end of the growth period, the root systems which had developed in all 36 pots were carefully inspected. Typical examples are shown in the accompanying illustration. Differences in top growth were accompanied by differences in root distribution and development. In all cases of great irregularity there were parallel irregularities in the quantity of

roots growing along the wall of the pot, between the pot and the mass of synthetic soil. In the comparable five treatments where the same Amberlite mixture had been irrigated with 0.03M NaCl, roots grew profusely throughout the mass of "soil." In the absence of NaCl only those roots that managed to get to the pot wall could grow well; the others remained abnormally dwarfed, and plants with only this type of roots grew poorly. The pots used were the same as those described earlier, they were lined with asphalt paint which has been shown to be inert and impermeable as used in the culture of plants.

As soon as a plant root reached the wall of the pot, part of its surface was protected from adverse contact with the Amberlite mixture, and it grew and functioned normally. Frequently solid layers of roots were developed, showing that roots could grow well between other roots. In fact, they grew better in such exposures than imbedded in the mass of Amberlite mixture. In the absence of contact with the Amberlite, the growth and function of roots seemed to be normal even though all of the nutrient ions were supplied by the Amberlite. It hardly seems possible, therefore, that the primary difficulty could be the unavailability of calcium and magnesium as such.

On the basis of these three points, it may be concluded that contact effects were playing an important role in the investigation reported. The number of contacts and the charge on the particles were both involved. A critical electrolyte level probably associated with the particle charge is indicated. In the range 0.01–0.03M concentration there is less adverse effect than in lower concentrations.

# CHEMICAL COMPOSITION OF THE COLLOIDAL CLAY FRACTION OF SOME SOLODI SOILS OF MINNESOTA<sup>1</sup>

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The solodi soils are an intrazonal group of soils usually found in association with the chernozem, chestnut, or brown zones under an arid, semiarid, or sub-humid climate. They occur in such association in Minnesota, commonly in slight depressions, although they may be found on level or nearly level terrain. Theories of their formation have been advanced chiefly by Russian investigators, but their morphology and genesis have not been too clearly determined thus far. It has been postulated that the solodi soils represent an advanced stage in the evolution of alkali soils from solonchak to normal soils. If, for some reason or other, an improvement in drainage of a saline soil should occur, then it is thought that removal of excess salts from the very salty solonchak results in a solonetz, which through further leaching becomes a solodi. From the acid solodi soil may then evolve a so-called normal soil, which has been replenished with bases from the subsoil by vegetation.

A number of workers have studied the colloidal materials from representative profiles of the major soil groups and have revealed significant differences in the chemical composition of these colloids. In other words, an analysis of the colloidal fraction of a soil will aid in determining to which group the soil belongs.

The present study is concerned with information on the colloidal material extracted from solodi soils in an attempt to categorize this intrazonal group on the basis of the chemical composition of the colloidal clay fraction. It was thought that the characteristics of these soils might be more clearly elucidated by such an investigation. The soils used have been identified as solodi by Rost and Maehl (24).

The literature pertaining to the chemical composition of soil colloids in relation to soil groups has been fairly well summarized by several workers (10, 22, 23). On the basis of the available information on the colloidal materials from the major soil groups, it appears that each group has very definite and distinctive characteristics as revealed by an analysis of the fine clay particles. Thus, different soil-forming processes produce colloidal fractions of differing chemical composition (1).

## MATERIALS AND METHODS

### *Description of the soils*

Soil samples, which represent six profiles under investigation, were obtained from Wilkin and Norman Counties in the Red River Valley of Minnesota. They

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are a degraded phase of Fargo clay and have been developed on lacustrine deposits.

The morphology of the soils used in this study is characterized by a dark brown to black or dark gray, compact, slightly lamellar to granular  $A_1$  horizon below which there is a light gray to ashy gray, lamellar, friable  $A_2$  horizon. The  $A_1$  varies from 4 to 8 inches in depth, and the  $A_2$  horizon ranges about 4 to 6 inches. The upper part of the B horizon is dark gray to dark olive-gray or black, with a coarse granular to fine blocky structure and a tendency to vertical cleavage. The lower part of the B horizon is similar to the upper but somewhat lighter in color and it does not have the tendency to vertical cleavage. The B horizon, in general, is compact, waxy and very sticky when wet, hard when dry. This horizon grades into a light olive-gray or buff-colored, more or less structureless C horizon which is less sticky and waxy than the material above it. The A and B horizons have an acid reaction, whereas the C may be neutral or slightly alkaline.

### Methods

The material with an equivalent diameter of  $0.5\ \mu$  and less was separated from the samples of soil with the aid of a Sharples supercentrifuge. The  $0.5\ \mu$  upper limit was chosen, since work on fine soil material indicates that particles up to this size exhibit essentially the characteristics of colloids.

The details of the procedure have been adapted from methods proposed by Hauser and Reed (16), Bradfield (3), Bray *et al.* (4), and Fry *et al.* (14), and is briefly as follows:

The soil sample was dispersed in distilled water and passed through a 300-mesh screen. The material passing through the screen plus washings usually approached a ratio of 1 part soil to 25 parts water. This suspension was fed at the rate of 450 ml. per minute into a Sharples supercentrifuge, the bowl of which rotated at 10,194 revolutions per minute.

The liquid obtained from the centrifuge was passed through Pasteur-Chamberland filters and finally evaporated to dryness on the steam plate. The material remaining on the inside of the centrifuge bowl was redispersed, with the clear liquid from the filters, and run through the same process as before. This was repeated ten times for each sample. The fine clay obtained from the ten filtrations was combined into one sample and evaporated to dryness.

Methods commonly used in the analysis of soils and silicate rocks were employed in this investigation.

The cations adsorbed on the exchange complex were extracted with 1 *N* ammonium acetate solution according to Peech (21).

Total exchange capacity was calculated from a colorimetric determination of adsorbed ammonia by direct Nesslerization (21).

The individual cations were determined by common analytical procedures, and the hydrogen was calculated by difference.

## RESULTS

*Chemical analysis of the colloids*

The chemical analyses, as well as other relevant data, are shown in table 1. The percentages of colloid are based on the air-dry weight of the soil; the organic matter and loss of ignition figures are based on the oven-dry weight of the colloid; the percentages of the various oxides are based on the oven-dry weight of the colloid less the organic matter. This method of expression gives a better comparison of the composition of the inorganic colloidal materials, since the effect of the organic matter is removed.

The results shown in table 1 reveal great uniformity in the chemical composition of the colloidal clay fractions.

The percentages of colloid (table 1) do not represent the total colloidal fraction (less than  $0.5 \mu$ ) in the soil, because even after ten times through the centrifuge, the liquid showed some opalescence. These values do account, however, for the major portion of the fine clay, and they are at least comparable. The A horizon contains the least amount of colloid of the three horizons, and the B appears to contain the most. Organic matter has diluted the products of weathering, and the inorganic colloidal clay content on a percentage basis has decreased in the A horizon. Some downward movement of fine material has taken place, resulting in an accumulation in the B horizon.

The various profiles show a marked similarity in organic matter content: a high percentage in the  $A_1$  horizon, a rather rapid decrease to the  $A_2$  horizon, and a more gradual and uniform decline to the C horizon.

The percentages of combined water in the colloids range from 5.05 per cent to 6.53 per cent with no trends revealed within the profiles. Combined water represents essentially water of hydration, and previous treatment will have considerable influence upon the amount found in the colloidal materials.

The amounts of silica contained in the colloidal material range from 54.49 to 60.01 per cent. This relatively high silica content seems to be characteristic of soils developed under an arid or semiarid climate, as suggested by some workers (5, 20). The higher percentage in the A horizon indicates a removal of sesquioxides from this layer, but this removal has not been extensive in any case.

The six profiles are similar with respect to their alumina content, the tendency being toward a greater amount in the B horizon than in either the A or the C horizons. The increase of alumina in the B horizon would give merit to the suggestion made above that some removal of sesquioxides has occurred from the surface horizon. This leaching of sesquioxides down the profile is characteristic of solodi soils according to Gedroiz (15).

The amount of iron oxide appears to increase with depth, although this does not hold for all profiles. The iron has been leached from the surface to a greater degree than the alumina, but there is no decided accumulation at lower depths.

There is a marked similarity among the profiles in their titanium content. Apparently  $TiO_2$  accumulates in the B horizon in podzol soils and other zonal

TABLE 1

*Chemical constituents of colloidal material extracted from horizons of six solodi profiles*

SAMPLE NUMBER	PROFILE NUMBER AND HORIZON	DEPTH	COLLOID	ORGANIC MATTER	LOSS ON IGNITION	COMBINED WATER	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O
		inches	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
31061-2	1-A <sub>1</sub>	0-8	9.49	14.33	18.99	5.44	58.81	18.85	8.19	0.62	.344	2.89	2.67	0.22	2.38
31063-4	A <sub>2</sub>	9-16	6.05	5.73	10.62	5.19	60.01	19.45	8.81	0.64	.115	1.54	2.46	0.34	2.14
31065	B <sub>1</sub>	17-20	22.14	2.64	8.24	5.75	58.51	19.52	9.18	0.53	.061	1.37	2.71	0.23	2.09
31066-7	B <sub>2</sub>	21-28	26.45	2.33	8.23	6.04	57.93	19.67	9.38	0.51	.073	1.39	2.87	0.33	1.81
31068	BC	29-32	26.65	1.80	7.20	5.50	57.99	18.71	10.70	0.52	.096	1.39	3.00	0.20	2.42
31069	C	33-	23.65	1.40	6.90	5.57	57.63	19.05	10.16	0.55	.119	1.56	3.02	0.45	2.04
31070	2-A <sub>1</sub>	0-6	11.68	12.54	17.89	6.12	57.74	18.32	8.64	0.63	.325	2.22	2.71	0.54	2.69
31071	A <sub>2</sub>	7-12	7.62	6.01	10.76	5.05	58.38	19.79	9.31	0.64	.155	1.57	2.45	0.37	2.93
31072	B <sub>1</sub>	13-16	23.57	2.62	8.43	5.97	56.25	19.95	9.63	0.51	.077	1.26	2.84	0.33	2.56
31073-4	B <sub>2</sub>	17-24	24.39	2.30	7.92	5.75	56.80	19.85	10.33	0.52	.082	1.23	2.90	0.69	1.75
31075-6	BC	25-32	22.55	1.60	7.02	5.51	57.33	19.50	10.41	0.54	.119	1.25	2.92	0.49	1.87
31077	3-A <sub>1</sub>	0-6	9.35	12.10	16.63	5.15	59.61	19.26	7.77	0.69	.367	1.63	2.35	0.39	2.63
31078	A <sub>2</sub>	7-10	16.32	3.82	9.40	5.80	56.90	20.92	9.07	0.61	.109	1.21	2.59	0.48	2.65
31079	B <sub>1</sub>	11-14	29.31	2.20	8.50	6.44	55.42	21.68	9.66	0.55	.084	1.26	2.73	0.33	2.84
31080-1	B <sub>2</sub>	15-22	31.75	1.98	8.35	6.50	55.32	20.78	10.34	0.56	.074	1.25	2.78	0.24	2.60
31082-3		23-30	29.56	1.56	7.29	5.82	55.97	20.96	9.50	0.59	.086	1.33	3.00	0.20	2.87
31084	BC	31-34	21.81	1.41	6.96	5.63	56.90	20.11	9.68	0.56	.130	1.52	2.86	0.29	3.07
31085	C	35-38	19.91	1.29	6.89	5.67	56.64	21.53	8.82	0.57	.155	1.84	2.92	0.29	2.09
31086-7	4-A <sub>1</sub>	0-8	10.15	11.77	17.34	6.31	56.35	19.01	9.45	0.62	.330	1.79	2.61	0.40	3.48
31088	A <sub>2</sub>	9-12	12.96	4.74	10.51	6.06	54.72	21.52	8.60	0.61	.144	1.43	2.57	0.20	2.35
31089	B <sub>1</sub>	13-16	21.61	2.42	8.69	6.42	54.49	21.78	10.65	0.57	.087	1.22	2.68	0.20	2.08
31090-1	B <sub>2</sub>	17-24	25.72	1.32	7.76	6.53	54.65	19.93	11.07	0.57	.081	1.25	2.89	0.22	2.08
31092	BC	25-28	23.78	1.27	6.84	5.62	54.72	19.82	10.73	0.59	.082	1.25	2.81	0.22	2.08
31093-4	C	29-36	24.47	0.98	7.29	6.37	55.32	19.54	10.80	0.59	.109	1.32	2.90	0.10	2.38
31095	5-A <sub>1</sub>	0-6	11.69	11.76	16.40	5.26	58.24	17.09	9.45	0.70	.405	1.74	2.69	0.24	2.71
31096	A <sub>2</sub>	7-11	15.64	4.42	9.72	5.54	56.24	19.30	9.74	0.67	.187	1.24	2.81	0.27	2.56
31097	B <sub>1</sub>	12-15	25.12	2.40	7.67	5.40	54.96	22.22	8.69	0.57	.103	1.16	3.15	0.21	2.90
31098-9	B <sub>2</sub>	16-23	25.84	2.39	7.58	5.32	55.22	20.12	10.15	0.56	.084	1.25	3.26	0.24	2.93
31100	BC	24-27	25.01	2.22	7.68	5.58	55.82	20.01	9.06	0.60	.107	1.40	3.30	0.22	2.40
31101-2	C	28-35	21.68	1.53	7.54	6.10	54.71	19.65	11.46	0.61	.145	1.75	3.33	0.24	2.43
28040	6-A <sub>1</sub>	0-4	8.53	8.96	14.72	6.11	55.26	19.89	8.04	0.61	.289	2.08	2.69	0.33	2.32
28041		5-8	7.56	12.34	17.64	6.05	56.03	19.83	8.92	0.65	.373	1.68	2.44	0.36	2.04
28042	A <sub>2</sub>	9-14	7.26	6.20	11.26	5.39	57.16	19.58	8.65	0.72	.142	1.54	2.39	0.31	2.29
28043	B <sub>1</sub>	15-18	22.49	2.75	8.20	5.60	55.82	21.04	9.76	0.55	.066	1.48	2.72	0.27	2.03
28044-5	B <sub>2</sub>	19-26	19.13	3.23	8.53	5.48	55.82	21.81	8.84	0.60	.068	1.60	2.74	0.26	2.49
28046-7	BC	27-34	20.03	3.10	8.58	5.65	55.69	20.14	9.37	0.61	.077	1.60	2.79	0.28	2.52
28048	C	35-38	24.56	1.59	7.15	5.65	56.66	20.16	9.46	0.61	.126	1.49	2.93	0.29	2.47

types but in the A horizon of laterites and lateritic soils (19), and also in the A horizon of the intrazonal soils under discussion.

There is good agreement both as to amounts of phosphorus and the distribution of this element throughout all the profiles. The  $A_1$  has a higher percentage of  $P_2O_5$  than the other horizons. This may be attributed to the high organic matter content of the surface horizons in which much of the phosphorus may occur in organic combination. All profiles show an increase of this element in the C horizon. The distribution of phosphorus in the profile may be explained by the vegetation's drawing on the reserves of this element in the B horizon and returning it to the surface as plants decay.

The calcium content has a rather wide range, especially in the  $A_1$  horizon. The trend is similar in all profiles, in that the CaO decreases with depth to the lower B and increases somewhat in the C horizon. A similar explanation to that for the distribution of phosphorus may be advanced for calcium, namely, that the vegetation returns it to the surface.

The magnesium content exceeds that of calcium, as shown in table 1. Joffe (19) points out that in a solodi there is a movement of magnesium downward in the profile, which results in a higher content of exchangeable magnesium at lower depths. The values for total magnesium indicate some accumulation of MgO in lower horizons.

The sodium content of these colloids is relatively low and variable, ranging from 0.10 to 0.69 per cent. Though these figures are higher than those reported by Caldwell and Rost (10) for colloids extracted from prairie, chernozem, and gray-brown podzol soils, they are not exceptionally high.

The amount of potassium present in the soil colloids is comparable to that of magnesium and is relatively high. There are variations within the profiles as well as among them, but there seems to be no definite order to these differences.

#### *Cation-exchange data*

The total exchange capacity and the millequivalents of the exchangeable cations for the colloids from three profiles are shown in table 2. The total exchange capacity is relatively high, that of the  $A_1$  horizon being higher than that of the remainder of the profile. The high capacity of the  $A_1$  horizon can be attributed to the greater amount of organic matter in this layer, since organic colloids are recognized as having a higher exchange capacity than inorganic (2). Hydrogen is the principal cation on the complex but calcium is nearly as prominent. The amount of exchangeable magnesium is only about one half that of the exchangeable calcium, and the exchangeable sodium, potassium, and manganese are low. There is a marked similarity in the three profiles and a noticeable uniformity within each profile in regard to total exchange capacity and to individual cations.

In table 3 are given the total percentages of the bases in the colloid and the percentages of these total bases that occur in nonexchangeable form. The determination of the exchangeable cations is useful in figuring the true silica-total base ratio and also is an aid in identifying the clay minerals present.

A few points revealed by these data (table 3) are worthy of note. Apparently the major portion of the calcium (91 to 100 per cent) exists in the exchangeable



TABLE 2

*Total exchange capacity and exchangeable cations of colloidal material from horizons of three solodi profiles*

PROFILE NUMBER AND HORIZON	TOTAL EXCHANGE CAPACITY	EXCHANGEABLE CATIONS					
		Ca	Mg	Na	K	Mn	H
	<i>m.s./100 gm.</i>	<i>m.s./100 gm.</i>	<i>m.s./100 gm.</i>	<i>m.s./100 gm.</i>	<i>m.s./100 gm.</i>	<i>m.s./100 gm.</i>	<i>m.s./100 gm.</i>
1-A <sub>1</sub>	97.5	40.1	15.2	0.4	3.3	0.4	38.1
A <sub>2</sub>	81.2	23.7	11.7	1.0	4.7	0.4	39.7
B <sub>1</sub>	75.5	22.3	12.1	0.6	4.0	0.2	36.3
B <sub>2</sub>	80.5	22.9	12.4	1.1	4.1	0.1	39.9
BC	75.7	23.1	12.8	1.1	4.3	0.1	34.3
C	76.5	25.4	11.0	1.1	4.3	0.1	34.6
2-A <sub>1</sub>	98.7	31.3	11.7	0.7	3.9	0.5	50.6
A <sub>2</sub>	83.7	24.7	10.3	0.9	3.4	0.5	43.9
B <sub>1</sub>	75.5	22.8	12.2	1.0	3.8	0.2	35.5
B <sub>2</sub>	76.0	22.2	12.3	0.9	3.5	0.1	37.0
BC	73.5	22.1	11.4	2.3	3.9	0.1	33.7
3-A <sub>1</sub>	83.7	25.4	9.9	1.1	2.3	0.5	44.5
A <sub>2</sub>	71.5	22.0	9.0	1.0	3.3	0.4	35.8
B <sub>1</sub>	75.5	22.8	10.3	0.9	3.9	0.1	37.5
B <sub>2</sub>	75.5	23.1	9.8	1.2	4.7	0.1	36.6
	79.0	24.0	10.0	1.0	3.4	0.1	40.5
BC	73.5	24.4	9.6	0.4	3.8	0.1	35.2
	77.5	30.1	9.0	2.2	3.1	0.1	33.0

TABLE 3

*Total bases in colloid fractions (from table 1), and percentages of these totals that are nonexchangeable*

PROFILE NUMBER AND HORIZON	TOTAL BASES				PROPORTION OF TOTAL BASES NONEXCHANGEABLE			
	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1-A <sub>1</sub>	2.89	2.67	0.22	2.38	9.00	73.41	95.45	92.86
A <sub>2</sub>	1.54	2.46	0.34	2.14	8.44	79.67	91.18	89.25
B <sub>1</sub>	1.37	2.71	0.23	2.09	6.57	81.55	91.30	90.91
B <sub>2</sub>	1.39	2.87	0.33	1.81	5.75	82.23	90.91	89.50
BC	1.39	3.00	0.20	2.42	5.04	82.33	85.00	91.73
C	1.56	3.02	0.45	2.04	7.69	85.10	93.33	90.20
2-A <sub>1</sub>	2.22	2.71	0.54	2.69	9.46	80.07	96.30	93.31
A <sub>2</sub>	1.57	2.45	0.37	2.93	5.73	82.04	91.89	94.20
B <sub>1</sub>	1.26	2.84	0.33	2.56	....	82.39	90.91	92.97
B <sub>2</sub>	1.23	2.90	0.69	1.75	....	82.41	91.30	90.86
BC	1.25	2.92	0.49	1.87	....	83.90	85.71	77.54
3-A <sub>1</sub>	1.63	2.35	0.39	2.63	1.28	80.85	92.31	95.44
A <sub>2</sub>	1.21	2.59	0.48	2.65	....	85.71	93.75	93.96
B <sub>1</sub>	1.26	2.73	0.33	2.84	....	84.61	90.91	93.66
B <sub>2</sub>	1.29	2.89	0.22	2.73	....	85.81	81.82	93.04
BC	1.52	2.86	0.29	3.07	8.55	86.01	96.55	94.14
C	1.84	2.92	0.29	2.09	7.06	87.67	75.86	92.82

form. Approximately 80 per cent of the magnesium, 90 per cent of the sodium, and 90 per cent of the potassium occur in the nonexchangeable form and thus may be considered essential constituents of the clay minerals.

### *Derived data*

Jenny (18) has pointed out the advantages of expressing chemical data as molecular values and also has given a list of ratios that have been used by soils workers. These ratios may be calculated from chemical analyses of the whole soil or the colloidal fraction. Only six ratios were calculated in this study, as shown in table 4. The authors have not seen the ratio of silica to nonexchangeable bases reported in the literature. Its significance will be discussed later.

The ratios of silica to sesquioxide are relatively wide for all profiles and all horizons. In general, the A horizon has a wider ratio than any layer below. This substantiates the suggestion made above that there has been some concentration of silica in this horizon. These values are for the most part higher than averages given by Reifenberg (22) for several zonal groups and those reported by Byers (8).

The silica-alumina ratios are relatively wide in comparison to those reported by Byers *et al.* (9) for the major soil groups. So far as can be indicated from the silica-alumina ratios, some alumina has been removed from the A horizon with some increase of this element in the B horizon.

The ratios of silica to iron oxide are relatively wide in comparison to those reported by others (9). There is a narrowing of the ratios with depth, especially from the A to the B horizon. Apparently iron has been removed from the A horizon with some accumulation in the B.

The iron oxide-alumina ratios indicate that iron has been removed from the A horizon to a greater degree than has the alumina.

The bases used in calculating the silica-total base ratios were calcium, magnesium, sodium, and potassium. These ratios range from 6.30 to 8.55 and are similar in value to those reported by others for some zonal soils (9, 10).

Since the bases used in the ratios above represent exchangeable and non-exchangeable forms, they do not represent the bases actually making up an integral part of the clay mineral crystals. To obtain some indication of the silica-base relationships in the clay minerals the ratios presented in the column to the extreme right of table 4 were calculated. The nonexchangeable fraction of the bases was used in the calculation. There does not appear to be any definite order for these ratios, which range from 9.61 to 13.10. All values are greater than any silica-base ratios reported in the literature.

### DISCUSSION OF RESULTS

It would seem that the factors of climate, parent material, vegetation, relief, and age, which contribute to the formation of the various soils, are responsible for the production of colloidal materials which are different in composition and characteristics for each particular soil. The colloidal materials of the major soil groups of the world seem to have a distinctive and characteristic

chemical composition. Data reported by Byers and Anderson (7) and others (6, 12, 13, 17) have led them to suggest that perhaps even soil series may be dif-

TABLE 4  
*Molecular ratios of the soil colloids*

PROFILE NUMBER AND HORIZON	$\frac{\text{SiO}_2}{\text{K}_2\text{O}}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Fe}_2\text{O}_3}$	$\frac{\text{Fe}_2\text{O}_3}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{BASES}^*}$	$\frac{\text{SiO}_2}{\text{BASES}^\dagger}$
1-A <sub>1</sub>	4.14	5.29	19.06	.277	6.67	12.21
A <sub>2</sub>	4.06	5.23	18.08	.289	8.55	13.10
B <sub>1</sub>	3.91	5.08	16.94	.300	8.28	12.17
B <sub>2</sub>	3.83	4.99	16.41	.304	8.00	11.75
BC	3.85	5.26	14.41	.346	7.52	10.86
C	3.83	5.13	15.07	.340	7.29	10.40
2-A <sub>1</sub>	4.11	5.34	17.74	.301	6.67	10.41
A <sub>2</sub>	3.85	5.00	16.67	.300	7.72	11.26
B <sub>1</sub>	3.65	4.78	15.52	.308	7.46	10.61
B <sub>2</sub>	3.65	4.86	14.64	.332	7.68	10.94
BC	3.72	4.98	14.64	.341	7.79	11.50
3-A <sub>1</sub>	4.17	5.25	20.39	.257	8.17	12.40
A <sub>2</sub>	3.61	4.61	16.69	.277	7.78	10.66
B <sub>1</sub>	3.37	4.33	15.24	.284	7.34	10.20
B <sub>2</sub>	3.49	4.55	15.03	.303	7.31	10.13
BC	3.67	4.80	15.63	.307	6.99	9.61
C	3.47	4.38	16.76	.261	7.01	10.47
4-A <sub>1</sub>	3.82	5.03	15.84	.317	6.71	
A <sub>2</sub>	3.43	4.31	16.92	.255	7.75	
B <sub>1</sub>	3.35	4.45	13.60	.312	7.97	
B <sub>2</sub>	3.43	4.65	13.12	.354	7.61	
BC	3.48	4.68	13.56	.345	7.75	
C	3.55	4.80	13.62	.353	7.51	
5-A <sub>1</sub>	4.27	5.78	16.37	.353	7.44	
A <sub>2</sub>	3.74	4.94	15.34	.322	7.57	
B <sub>1</sub>	3.36	4.19	16.82	.249	6.86	
B <sub>2</sub>	3.52	4.65	14.45	.322	6.66	
BC	3.67	4.73	16.36	.289	6.93	
C	3.44	4.72	12.68	.372	6.30	
6-A <sub>1</sub>	3.73	4.75	17.48	.272	7.39	
A <sub>2</sub>	3.86	4.95	17.57	.282	8.20	
B <sub>1</sub>	3.47	4.50	15.20	.296	7.75	
B <sub>2</sub>	3.45	4.34	16.77	.259	7.31	
BC	3.61	4.69	15.79	.297	7.22	
C	3.67	4.76	15.91	.299	7.25	

\* Total Na<sub>2</sub>O, K<sub>2</sub>O, MgO, and CaO.

† Nonexchangeable Na<sub>2</sub>O, K<sub>2</sub>O, MgO, and CaO.

ferentiated on the basis of the chemical nature of the colloidal material in soils. The colloidal material from intrazonal soils, however, has not been investigated

to any great extent, and there are few data available except for a few profiles of solonetz and alkali soils. The authors have been unable to obtain any literature reporting chemical analysis of the colloids of solodi soils, but it is possible to compare the chemical composition of the solodi soils studied here with other zonal and intrazonal soils and indicate similarities and differences which may help to further categorize these soils.

TABLE 5  
*Average molecular ratios for various soil groups*

SOIL GROUP	HORIZON	$\frac{\text{SiO}_2}{\text{R}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{Fe}_2\text{O}_3}$	$\frac{\text{Fe}_2\text{O}_3}{\text{Al}_2\text{O}_3}$	$\frac{\text{SiO}_2}{\text{BASES}}$
Laterites	A	0.80	1.01	3.68	.277	20.90
	B	1.51	1.95	4.56	.324	24.63
	C	1.66	1.87	15.00	.124	96.00
Red-yellow podzolic	A	1.46	1.72	8.95	.208	17.09
	B	1.39	1.65	7.10	.250	29.22
	C	1.42	1.75	6.98	.272	42.56
Brown podzolic	A	1.61	2.10	7.35	.318	8.37
	B	0.66	0.82	3.64	.225	9.38
Gray-brown podzolic	A	2.13	2.66	10.67	.258	9.23
	B	2.10	2.75	9.00	.351	10.94
	C	2.09	2.70	9.94	.297	12.57
Podzols	A	3.28	3.93	19.76	.226	11.78
	B	1.42	2.09	5.44	.404	8.81
	C	2.07	3.28	8.52	.369	5.75
Prairie	A	2.66	3.61	10.24	.354	7.25
	B	2.73	3.60	10.26	.362	7.85
	C	2.63	3.68	9.24	.296	7.99
Chernozem	A	2.93	4.38	12.37	.372	6.92
	B	3.28	4.23	12.72	.389	6.68
	C	3.25	4.88	13.72	.403	6.88
Solodi	A	3.90	5.04	17.34	.292	7.55
	B	3.54	4.61	15.31	.302	7.52
	C	3.64	4.82	14.92	.324	7.28

As pointed out in the experimental results, molecular ratios offer a convenient and concise method of expressing analytical data. Average ratios for the several great soil groups have been calculated, therefore, from data in the literature and are presented in table 5. The values shown do not represent the means of the same number of individual ratios for each. A few represent only single determinations, but most of them are means of from two to nearly thirty ratios. It is realized that averages of a large number of values are not very significant

unless the range of the individuals is known. In most cases, however, the ratios for the same soil type and same horizon were markedly similar, with the possible exception of podzols, which showed some variation in different profiles but the trends within the profile of which were fairly similar.

Table 5 indicates that the major soil groups possess colloids with characteristic chemical compositions. The solodi group, when compared with the zonal soil types, appears to be not unlike the chernozem in so far as the actual values of the ratios are concerned. However, dissimilarities in trends within the profile are readily observed. For instance, the solodi group has a narrowing of the silica-sesquioxide ratio in the B horizon which is more like the podzol colloids, although the latter show it to a much greater degree, of course. Further evidence of similarity in the podzol and solodi profiles can be seen in the silica-alumina and the silica-iron oxide ratios. These similarities pertain to trends throughout the profiles rather than the actual values shown. The aforementioned facts suggest a similarity between the solodization and podzolization processes substantiating the theories of Gedroiz (15).

There are other points concerning the ratios of the solodi soils worthy of note. The silica-sesquioxide and silica-alumina ratios are in general wider in the solodi than in any other group of soils shown in table 5. This substantiates what others (5, 11, 18) have indicated, namely, that conditions of limited rainfall induce the formation of colloids with wide silica-sesquioxide and wide silica-alumina ratios.

#### SUMMARY

The colloidal material (less than  $0.5 \mu$  in diameter) was extracted from 37 samples of soil representing six solodi profiles. The material so extracted was subjected to a fairly complete chemical analysis including base-exchange determinations. Various molecular ratios were calculated from the analytical data.

The amounts of colloid extracted suggested some eluviation of material from the surface layers. Illuviation in the B horizon was indicated by an increase in the colloid content of this layer.

The organic matter was noticeably high in the  $A_1$  horizon. It decreased rapidly to the  $A_2$  and declined gradually to the C horizon.

The combined water was remarkably uniform in all profiles and appeared to be relatively low.

The chemical analyses showed that the colloids contained approximately 56 per cent silica, 20 per cent alumina, 9.5 per cent iron oxide, and lesser amounts of titanium, phosphorus, calcium, magnesium, sodium and potassium.

Cation exchange data showed that hydrogen was the most abundant cation on the complex. The major portion of the calcium in the colloids apparently existed in the exchangeable form, whereas the opposite was true for the magnesium, sodium, and potassium.

Various molecular ratios, calculated from the analytical data, were discussed and were compared with ratios for other soil groups.

Several facts have been brought out by this study. The colloidal materials from the solodi soils seem to have somewhat distinctive characteristics. Though they are similar to the chernozem colloids in the values of many ratios, they are nevertheless more like the podzol or podzolic colloids in the trends within profiles.

The results obtained in this investigation, while indicative and suggestive, are not conclusive. Since only a relatively few profiles were studied, and those from a more or less limited area, many more experimental data on these soils from other regions are required to establish the distinctive characteristics of the solodi colloids.

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# THE EFFECTS OF CALCIUM FLUORIDE INCORPORATIONS UPON PLANT GROWTH, FLUORINE AND PHOSPHORUS UPTAKE, AND SOIL pH<sup>1</sup>

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Fluorine in soils has been attributed to occurrences of tourmaline, biotite, muscovite, and phlogopite, the micas, and to apatite and fluorite (6, 18, 21, 22, 24, 25). The element occurs in relatively meager proportions, however, in soils other than those derived from rocks of unusual apatite, or fluorophosphate, content. Fluoride increments come to the soil through the use of phosphatic fertilizers and insecticides (10) and through rainwaters (15).

Fluorine was virtually disregarded as a component of the soil system until recent concern as to possible effects of additive fluorides prompted studies that led to the adaptation of an analytical technic (16) prescribed by the A. O. A. C. (2). The fluorine occurrences in profiles of many types of soils were reported in a recent contribution on the apparent fate of fluorides carried by incorporations of fertilizers (21).

Soluble fluorides have been added to soils to determine effects upon plant growth (1, 5, 8, 26) and also for pest control (10, 23) as well as for effects upon the malting of grain (22). In some cases, the fluoride additions proved beneficial; in others they were of no effect; and in still others they proved detrimental (10), especially to germination (1, 3, 4, 8) and to the feeding value of the grain wastes from distilleries (22). As pointed out by Aso (1) and found at the Tennessee Station (10) however, incorporated soluble fluorides undergo substantial transition to equivalences of the less soluble fluoride of calcium. Hence, for soils having normal occurrence of reactive alumina, consideration of the effects of any probable input of fluorine is narrowed virtually to the behavior of an equivalence of calcium fluoride.

Recent contributions dealt with the possibility that fluorides carried by incorporations of superphosphate may exert an influence within the soil system (13, 14, 18, 20). One worker concluded that such an input of component fluorides proved injurious to the germination of corn on unlimed soil (19). Hart, Phillips, and Bohstedt (9) raised the question whether continuous fertilizer incorporations impart to forage crops a fluoride concentration toxic to livestock. No significant increase in percentage of fluorine content was found, however, in greenhouse crops from Tennessee soils that had been enriched by some 4.5 ton

<sup>1</sup> Paper read before the Fertilizer Section of the American Chemical Society at its 110th meeting at Chicago, September 9-11, 1946, and released by request for publication in this journal.

<sup>2</sup> These studies were conducted in collaboration with the Tennessee Valley Authority, departments of chemical engineering and agricultural relations. Acknowledgment is accorded H. S. Johnson, Jr., for the reported  $P_2O_5$  analyses.



of calcium fluoride through an incorporation of superphosphate equivalent to the aggregate of 500 successive 500-pound incorporations per acre (15). Since such an incorporation resulted in soil systems that were too acidic to admit of normal germination and immediate plant growth, additions of wollastonite beyond equivalence were made to offset the acidity of the superphosphate and also that of a control parallel of fluoride-free monocalcium phosphate. The heavy input of component calcium fluoride in the heavily superphosphated soil, therefore, had been supplemented by substantial proportions of readily available calcium in the forms of generated dicalcium phosphate and additive silicate, with a resultant build-up of calcium content that militated against dissolubility the fluoride carried by the incorporated superphosphate. That situation was avoided in the present pot culture study wherein substantial inputs of calcium fluoride were made to acidic soil without companion additions of other calcic materials. It seemed logical that such inputs would serve to indicate any effects that could be attributed to those smaller quantities of fluorides that are introduced when phosphatic fertilizers are incorporated at rational rates, either alone or with judicious usage of liming materials.

#### OBJECTIVES

An initial intent of the experiment reported in this paper was to ascertain whether substantial incorporations of calcium fluoride would serve as sources of adequate supplies of nutrient calcium. It was intended to compare equivalent incorporations of calcium fluoride and calcium carbonate as registered by plant growth, fluorine uptake, and soil reaction in a soil known to be responsive to liming. The experiment was planned to ascertain whether additive calcium fluoride serves to (a) promote growth of nonlegumes and alfalfa, (b) increase the uptake of fluorine and influence phosphorus content in tops and in roots, and (c) affect soil pH. A corollary objective was to dispel any doubt that the higher fluorine analyses of roots that had been collected from experimentally phosphated soils of previous experiments were due to fluorine uptake rather than to contamination from adherent solids.

#### EXPERIMENTAL

The soil cultures were duplicated in 2-gallon glazed pots. The experimental technique has been described and the facilities utilized have been illustrated (17). Pulverized fluorspar and precipitated  $\text{CaF}_2$  were the additive fluorine materials, and limestone and two experimental calcium silicate slags, all of minus 100-mesh, were used as controls. Each of the five materials was incorporated separately at the rate of 2 tons  $\text{CaCO}_3$ -equivalence per acre surface. The two calcium fluoride materials were incorporated also at the  $\frac{1}{2}$ -ton rate. These two rates provided 1520-pound and 3040-pound inputs of fluorine per acre. Potassium sulfate was a constant addition at the rate of 370 pounds per acre surface. The five materials were incorporated without phosphate and with concentrated superphosphate (45 per cent  $\text{P}_2\text{O}_5$ ) that provided an 83-pound input of  $\text{P}_2\text{O}_5$ . The solid materials were incorporated into the upper half of soil just prior to the

initial seeding, but the ammonium nitrate top-dressings were made in solution. The upper and lower zones of soil were separated by means of a wire cloth disc, as shown in figure 1. This demarcation was provided so that root segments for analyses could be collected from a zone into which solid calcium fluoride had not been incorporated and thus would be deemed not contaminated with adherent particles of high fluorine content. The fluorine analyses of plant growth were made by the successive steps of incineration of  $\text{Ca}(\text{OH})_2$ -impregnated charges, steam distillation of fluoric gas from  $\text{HClO}_4$  solution of incinerates (12), and back titration of distillate by means of  $\text{Th}(\text{NO}_3)_4$  (7, 27).

#### RESPONSES BY SUDAN GRASS AND RYE GRASS

Sudan grass and rye grass were grown successively on Hartsells fine sandy loam. Response by each crop to each treatment is pictured in figures 2 and 3. Data of table 1 show crop growth as grams, dry weight, per pot; fluorine and  $\text{P}_2\text{O}_5$  contents of the tops, aggregate fluorine removals; and soil reactions after each crop. No fluoride addition induced any observable effect upon the germination of the Sudan grass. That crop showed no response to the fluoride incorporations

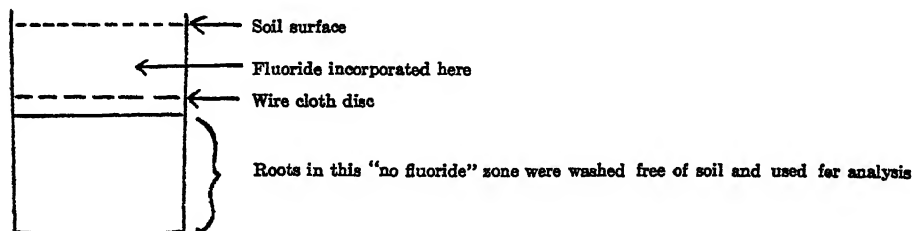


FIG. 1. DIAGRAM OF POT CULTURE

that were not supplemented by superphosphate, whereas it did respond to limestone and to the experimental slags, without additions of phosphate. The responses of Sudan grass to the four fluoride + superphosphate combinations (table 1 and fig. 2) were considerably less than the responses to the corresponding incorporations of limestone + superphosphate and to an experimental slag + superphosphate, as they were also less than the growth of 15.3 gm. per pot in the unpictured controls, which received superphosphate alone. Thus, in combination incorporations with calcium as either carbonate or silicate, superphosphate proved more effective than analogous combinations of superphosphate with calcium as fluoride. The ineffectiveness of this equivalent and *potentially* adequate supplement of calcium is probably attributable to its meager dissolvability and possibly to repressive effect upon phosphate "availability."

The incorporations of superphosphate tended to produce higher  $\text{P}_2\text{O}_5$  percentages in the plant, as well as larger crops, and hence larger removals of phosphorus, which are indicative of corresponding increases in removals of calcium. Although uptake of calcium was not a primal objective in the present experiment, the crops were analyzed for content of that element and for potassium content. The analyses demonstrated that the uptake of calcium was in parallel with

uptake of phosphorus and came partly from the added fluoride. Since adequacy of potassium was assured by the addition of its sulfate, the relationship of calcium to potassium in uptake was not deemed pertinent to the present treatise.

The order of response by the succeeding crop of rye grass, as well as the aforementioned relationship of calcium and phosphorus uptake, was much the same as that noted for the Sudan grass.

TABLE 1

*Effect of calcium fluoride incorporations upon growth and fluorine content of two successive nonlegumes and upon reaction of Hartsells soil*

INCORPORATIONS*				DRY WEIGHT— PER POT			P <sub>2</sub> O <sub>5</sub> CONTENT		FLUORINE CONTENT		AGGREGATE 2 CROPS		SOIL REAC- TION AFTER	
Material	CaCO <sub>3</sub> equiv.	F	P <sub>2</sub> O <sub>5</sub>	Sudan grass	Rye grass	Total	Sudan grass	Rye grass	Sudan grass	Rye grass	Dry weight	Fluorine re- moved	Sudan grass	Rye grass
	<i>tons</i>	<i>lbs.</i>	<i>lbs.</i>	<i>gm.</i>	<i>gm.</i>	<i>gm.</i>	<i>per cent</i>	<i>per cent</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>lbs./A.</i>	<i>lbs./A.</i>	<i>pH</i>	<i>pH</i>
None	..	....	....	7.3	0.5	7.8	0.23	0.23	....	....	....	....	4.4	4.0
CaF <sub>2</sub> , ppt.	2	1520	0	6.9	1.8	8.7	0.26	0.34	140	1,100	2,184	.74	5.2	4.7
			83	14.0	4.5	18.5	0.30	0.34	65	230	4,644	.49	5.3	4.9
	4	3040	0	6.9	1.6	8.5	0.23	....	130	600	2,134	.25	4.7	4.9
			83	11.6	4.5	16.1	....	0.39	170	330	4,042	.87	5.2	4.9
Fluorspar	2	1520	0	6.9	1.5	8.4	0.23	0.32	110	800	2,109	.49	5.0	4.7
			83	10.8	5.7	16.5	0.32	0.34	110	160	4,142	.53	5.1	4.9
	4	3040	0	7.3	1.4	8.7	0.23	....	140	1,000	2,183	.61	4.6	4.6
			83	12.2	3.3	15.5	0.31	0.34	110	180	3,890	.49	5.1	4.8
Exptl. slag†	2	0	0	11.9	2.7	14.6	0.27	0.32	2	23,865	.007	6.0	6.0	
			83	19.3	7.5	26.8	0.38	0.37	3	66,728	.026	6.7	6.6	
Exptl. slag‡	2	112	0	11.7	3.7	15.4	0.34	0.31	1	23,866	.005	6.4	6.6	
			83	18.1	9.5	27.6	0.39	0.37	2	56,928	.021	7.0	7.1	
Limestone	2	0	0	10.3	1.7	12.0	0.25	0.27	8	33,013	.022	7.0	6.6	
			83	19.0	5.2	24.2	0.33	0.37	5	36,074	.028	6.8	6.7	

\* The calcic materials were added at the specified rates per acre surface and were incorporated into the upper half of soil.

† Simulative of Wilson Dam slag, minus fluorine.

‡ Simulative of Wilson Dam slag, with inclusion of CaF<sub>2</sub>.

The cultures do not afford an absolute explanation as to why neither crop registered significant response to the calcium fluoride materials when the two forms were used alone. But, since there was no visual indication of deleterious effect to the germination of successive seedings—Sudan grass, rye grass, and alfalfa—calcium fluoride hardly could have developed a salt concentration specifically toxic to either of the crops. Apparently, the dissolvability of the fluorine

materials was not sufficient to provide an adequate supply of nutrient calcium and concomitant concentration of fluorine ions was not enough to induce fluoric toxicity. Apparently, also, the fluorides did not supply solute calcium in keeping with the  $\text{PO}_4$  enrichment afforded by the incorporations of superphosphate. Nevertheless, since 1 part of calcium fluoride by weight can induce the transition of 12 parts of tricalcium phosphate to fluorophosphate in mixtures outside the soil

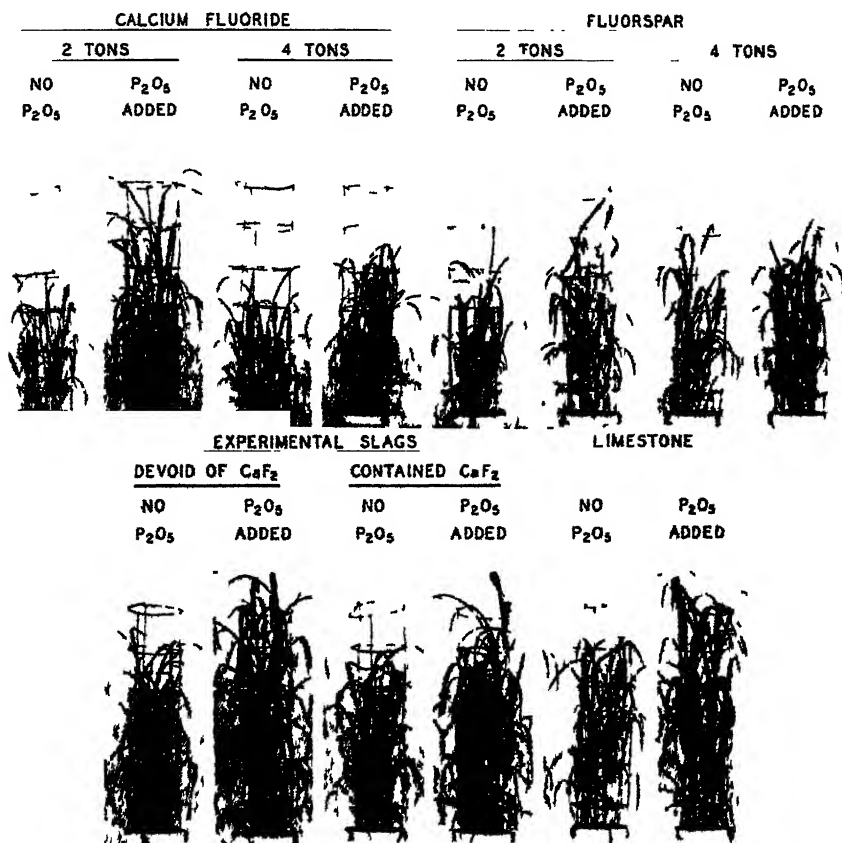


FIG. 2. COMPARATIVE EFFECT OF INCORPORATIONS OF PRECIPITATED CALCIUM FLUORIDE, FLUORSPAR, SLAGS, AND LIMESTONE ON GROWTH OF SUDAN GRASS

(11, 13, 14), the added fluoride may have exerted some adverse effect upon the efficacy of the added phosphate, during the growth of the Sudan grass in particular.

The fluorine analyses are expressed in terms of concentration in the dry plant and as aggregate removals of the element per acre. Incorporated alone, the fluoric materials brought about considerable increase in the concentration of fluorine in the Sudan grass, and still greater increases in the rye grass. It appears that both crops fed upon the 1520-pound and 3040-pound inputs of calcium

that were carried by the fluoride incorporations, although the plants may have fed also upon calcium supplied through replacement by the K of the liberal incorporation of  $K_2SO_4$ . The substantially higher concentrations of fluorine shown for the rye grass may be attributable to growth in soils that had become enriched in solute fluorides during the growth and the root decay of the preceding crop, or to greater inherent capacity of rye grass to assimilate fluoric compounds. The latter explanation seems the more probable, however, because of the relatively

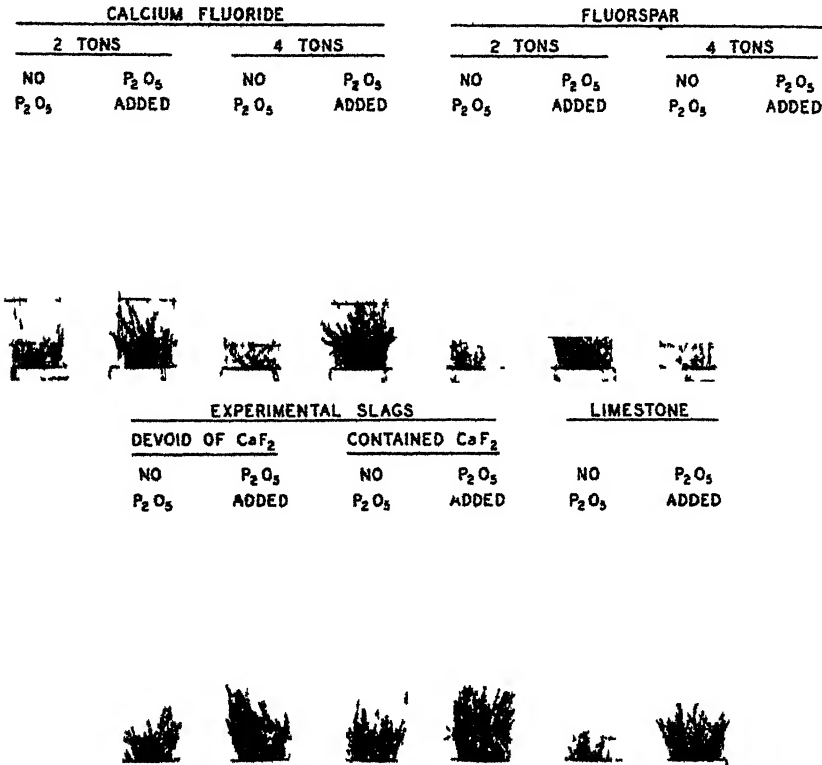


FIG 3 COMPARATIVE EFFECT OF INCORPORATIONS OF PRECIPITATED CALCIUM FLUORIDE, FLUORSPAR, SLAGS AND LIMESTONE ON GROWTH OF RYE GRASS

low concentration of fluorides that appeared in the succeeding alfalfa crop (table 2). Although the analyses register no consistent effect of additive superphosphate upon the concentration of fluorine that the Sudan grass derived from added calcium fluoride, they do show a decided decrease in the concentration of fluorine in the rye grass from the cultures into which both calcium fluoride and superphosphate had been incorporated.

Elevations in pH were noted after the first and second crops in the 16 cultures wherein a fluoric material had been incorporated, but such elevations were less than those induced by the  $CaCO_3$ -equivalent incorporations of either limestone

or experimental slag. Thus, a significant change in soil pH may be induced by a substantial input of a relatively insoluble salt, although the bulk of the additive material remains unchanged and hence effects no appreciable build-up of base within the soil complex and does not serve adequately as a nutrient carrier.

TABLE 2

*Effect of calcium fluoride incorporations upon growth and fluorine content of alfalfa following two nonlegumes and upon soil reaction*

INCORPORATIONS*						DRY WEIGHT TOPS	P <sub>2</sub> O <sub>5</sub> CONTENT		FLUORINE CONTENT		DRY WEIGHT OF CROP	FLUO- RINE RE- MOVED	SOIL REACTION AFTER ALFALFA
Material	Initial			For alfalfa			Tops	Roots	Tops	Roots			
	CaCO <sub>3</sub> - equiv.	F	P <sub>2</sub> O <sub>5</sub>	Lime- stone†	P <sub>2</sub> O <sub>5</sub>								
	tons	lbs.	lbs.	tons	lbs.	gm.	per cent	per cent	p.p.m.	p.p.m.	lbs./A.	lbs./A.	pH
None	..	.....	.....	.....	.....	nil	....	....	....	....	....	....	3.9
CaF <sub>2</sub> ‡	2	1520	0	0	0	nil	....	....	....	....	....	....	4.4
			0	2	0	3.5	0.41	....	12	....	879	.010	6.6
	2	1520	83	0	83	0.9	0.44	....	6	....	226	.001	4.7
			83	2	83	13.2	0.53	0.41	9	70	3,313	.030	7.0
CaF <sub>2</sub> ‡	4	3040	0	0	0	nil	....	....	....	....	....	....	4.6
			0	2	0	4.7	0.40	....	10	....	1,180	.012	6.7
	4	3040	83	0	83	2.0	0.44	....	38	....	502	.019	4.8
			83	2	83	13.8	0.55	0.41	12	70	3,464	.042	6.9
Exptl. slag§	2	0	0	0	0	4.5	0.39	....	4	....	1,130	.005	6.2
			83	0	83	10.4	0.46	0.33	8	15	2,610	.021	6.3
Exptl. slag	2	112	0	0	0	5.7	0.37	....	7	....	1,431	.010	6.7
			83	0	83	10.8	0.46	0.32	8	18	2,711	.022	6.5
Limestone	2	0	0	0	0	3.3	0.38	....	5	....	828	.004	6.4
			83	0	83	10.8	0.50	0.33	6	20	2,711	.016	6.6

\* The calcic materials were added at the specified rates per acre surface and were incorporated into the upper half of soil.

† All of the second liming additions were as limestone at the 2-ton rate.

‡ Mixture of the precipitated calcium fluoride and fluorspar cultures.

§ Simulative of Wilson Dam slag, minus fluorine.

|| Simulative of Wilson Dam slag, with inclusion of CaF<sub>2</sub>.

#### ALFALFA

#### Preparation of cultures

Since the two nonlegumes apparently could not derive sufficient nutrient calcium from the fluoride incorporations, it seemed certain that alfalfa would require additive calcium beyond that carried by those incorporations. The

experimental distinction between the two types of calcium fluoride was terminated, therefore, after the two nonleguminous crops of table 1 had been harvested, and the soils were processed prefatory to the seeding of alfalfa. Those cultures that had received a 2-ton incorporation of fluorspar alone were combined with those that had received a like incorporation of precipitated fluoride, and those that had received a corresponding input of calcium fluoride material and superphosphate were likewise combined. Those cultures that had received the 4-ton inputs of the two types of calcium fluoride alone and with superphosphate were combined in like manner. The four resultant composites afforded culture pairs that had received  $\text{CaF}_2$  at the 2-ton  $\text{CaCO}_3$ -equivalent rate (a) without  $\text{P}_2\text{O}_5$ , and (b) with an initial 83-pound input of  $\text{P}_2\text{O}_5$ , and also culture pairs that had received  $\text{CaF}_2$  at 4-ton  $\text{CaCO}_3$ -equivalent rate, (c) without  $\text{P}_2\text{O}_5$ , and (d) with the initial 83-pound input of  $\text{P}_2\text{O}_5$ . Second incorporations of superphosphate then were made to the composites (b) and (d), and each of the four soil composites was divided equally into four pots. Two pots of each quartette were continued as representative of fluoride additions without a liming material, whereas the other two pots were limed at the rate of 2 tone of  $\text{CaCO}_3$  per acre surface, the limestone incorporations being into the upper half of soil.

### *Response and uptake*

The crops of alfalfa, expressed as grams dry weight per pot, are recorded in table 2, along with the several values for  $\text{P}_2\text{O}_5$  content, fluorine content and removals, and terminal pH values. The responses are pictures by single pots in figure 4.

Alfalfa failed to grow on either the untreated soil or in those soils into which calcium fluoride had been incorporated *alone* at the 2-ton and 4-ton rates. The fluoride incorporations had exerted no visibly detrimental effect upon germination, but the seedlings did not develop into mature plants. Alfalfa did respond to sole incorporations of limestone, however, and to like incorporations of experimental calcium silicate slags. Moreover, alfalfa gave little response to the repetitive additions of superphosphate on those soils to which the 2-ton and 4-ton fluoride incorporations had been made before the growth of the preceding crops of Sudan grass and rye grass. The superphosphate proved decidedly beneficial, however, when supplemented by calcium in available form, the limestone + phosphate and slag + phosphate combinations having brought responses double those induced by the liming materials alone. Since no growth of alfalfa occurred in the cultures that received calcium fluoride alone at the 4-ton  $\text{CaCO}_3$ -equivalent rate, the small response of that crop to the joint incorporation of fluoride and superphosphate might be attributed to the calcium of the superphosphate, or to retardative effect of the superphosphate upon the "availability" of the calcium of the fluoride. Hence, again it appears that the fluoride failed to supply plant growth with adequate nutrient calcium.

The alfalfa responded alike to limestone and to the experimental slags, when these were incorporated singly, and also when incorporated jointly with superphosphate. Since the best response by alfalfa came from the combination of

limestone and the second addition of superphosphate that was sequential to the 2-ton and 4-ton incorporations of fluoride before the crop of Sudan grass, it appears that the limestone calcium altered any repressive tendency the additive fluoride may have exerted upon the preceding crops in their utilization of the incorporated phosphate.

In the absence of a crop of alfalfa on the untreated soil, the crops from the soils that had been either slagged or limestoned were deemed controls as to fluorine content. The only probably significant increase in the fluorine content

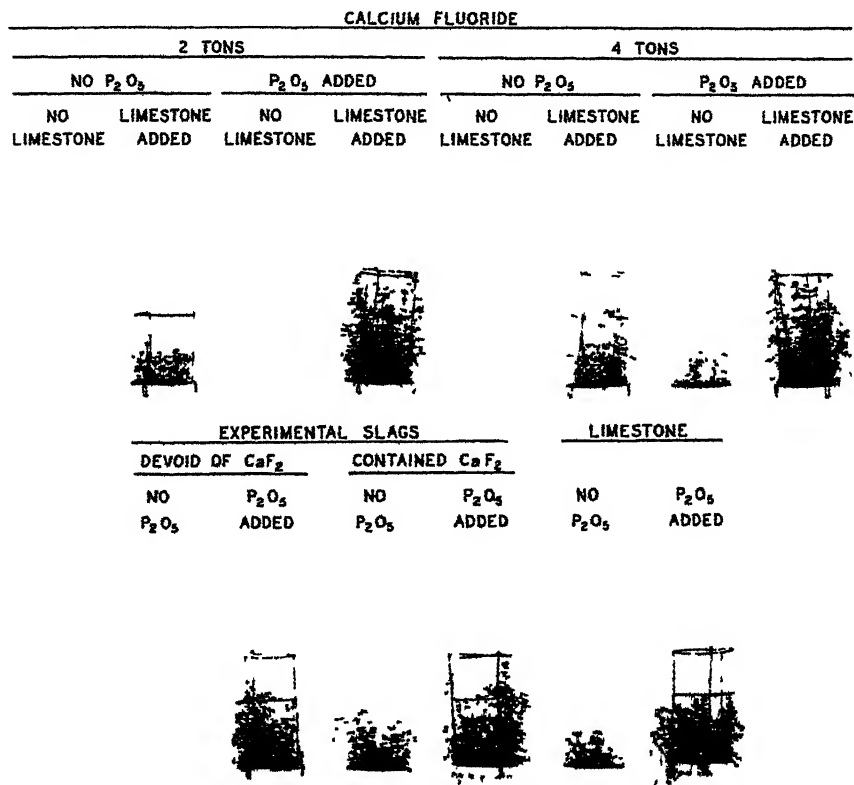


FIG. 4. COMPARATIVE EFFECT OF INCORPORATIONS OF PRECIPITATED CALCIUM FLUORIDE, FLUORSPAR, SLAGS, AND LIMESTONE ON GROWTH OF ALFALFA

of the tops was the one found for the 4-ton addition of  $CaF_2$  that had been supplemented with two incorporations of superphosphate.

The fractions of the alfalfa roots that were segregated in the demarcated zone of the unslagged and limestoned cultures were not adequate for replicated analyses for fluorine content. This was true also of the root growth in those cultures that received either limestone or slag without superphosphate. In each of the five cases where zonal root growth was such as to provide adequate analytical charges, fluorine concentration in the roots was beyond that found for



the corresponding above-ground growth. This finding is deemed conclusive, since the zonal sampling of the roots served to minimize the possibility of their mechanical contamination. The maximal concentration of 70 p.p.m. of fluorine in the alfalfa roots was found in those from the cultures that had received superphosphate and a fluoride material initially and had been rephosphated and limestoned prefatory to the seeding of alfalfa. Such concentration is several times that found for the alfalfa roots from the two phosphatings with either of the three liming materials and indicates that the enrichment came from the two fluoric materials.

Adequate analytical charges for determination of  $P_2O_5$  in both tops and roots were available in five of the seven pairings in table 2. In two of these pairings, the initial inputs of calcium fluoride and superphosphate had been followed by a second phosphating, with and without limestone, prior to the seeding to alfalfa. In the other three pairings, additions of either slag or limestone had been made initially, with or without superphosphate. The crops on the soils that had received calcium fluoride and a second input of superphosphate along with limestone were larger and were higher in  $P_2O_5$  content than the crops grown on the soils that had received identical fluoride and phosphate additions without the limestone supplement that was made to assure growth of the alfalfa. In every instance, the percentage of phosphorus in the top growth exceeded that in the roots, and superphosphate increased both growth and  $P_2O_5$  percentage in the three control pairings that were either limestoned or slagged.

The incorporated calcium fluoride continued to effect small, and probably significant, rises in pH. Further and substantial elevations in pH values were induced by the limestone incorporations in each of the four upper pairings of table 2. The three control pairings for the alfalfa cultures continued to show a distinct rise in pH from every incorporation of either slag or limestone, in consonance with the earlier effects shown for the corresponding pairings of Sudan grass and rye grass in table 1.

#### OBSERVATIONS AND CONCLUSIONS

Incorporated alone at the rates of 2 and 4 tons of  $CaCO_3$ -equivalence, calcium fluoride exerted no visible toxic effect upon the germination of Sudan grass, rye grass, or alfalfa, and caused no observable repression upon sequential seedling growth. No increase in crop growth was induced by any sole addition of calcium as fluoride, although appreciable growth increases were induced by the separate incorporations of calcium silicate and limestone.

Although the 2-ton and 4-ton inputs of calcium fluoride underwent hydrolysis to the extent of causing a significant elevation in pH, they apparently did not provide nutrient calcium sufficient to induce any increase in any of the three crops that were grown successively on the soil known to be responsive to liming. When incorporated alone in soil of low content of either active alumina or additive phosphates, calcium fluoride probably continues chiefly as such during the period of dissolution and outgo and probably exerts no great effect upon biochemical activities.

Since the experimental setup did not admit of the separation of the roots of the first two crops—Sudan grass and rye grass—their tops alone were available for fluorine analysis. Substantial uptake from the fluoride additions was registered by the increases in the fluorine content of Sudan grass and still more so by the fluorine present in the rye grass. The added fluoride also enhanced the fluorine content of the alfalfa roots.

The largest removal of fluorine was that equivalent to one of 0.87 pound from the 4-ton input of calcium fluoride and was accounted for jointly by the analyses of Sudan grass and rye grass in table 1. That fluorine removal represents only 0.057 per cent of the smaller input of 1,520 pounds of fluorine. Since virtually all the fluorine was residual in the unleached pots and yet caused no observable injury to germination and no visible toxic effect upon sequential plant growth, it seems logical to conclude that germination, crop nutrition, and feeding value would not be affected adversely by the 5- or 10-pound increments of fluorine carried by rational incorporations of fertilizers.

There might be a question whether lack of response to the joint incorporation of phosphate and fluoride and to a repetitive addition of phosphate without limestone is explainable as an inadequacy of nutrient calcium rather than a diminution in phosphate availability. But, since substantial increases in growth did result after the initial joint incorporation of fluoride and superphosphate had been supplemented by limestone, inadequacy of nutrient calcium is deemed the more plausible explanation.

In each of four pairs in table 1, fluorine concentration was higher in the rye grass grown on the soils that received fluoride without phosphate. This may be attributed singly or jointly to the several factors—smaller crops, cumulative dissolution of the added fluorides, or specific capacity for the utilization of calcium fluoride. The diminution in the occurrence of fluorine in the rye grass of the four companion units that received both fluorine and superphosphate initially may be due to the fact that the crop was growing on soil wherein solute fluoride had increased after the additive phosphate had exerted its capacity to react with that solute in the formation of calcium fluorophosphate.

#### CONCLUSIONS

The findings point to several conclusions. Additive calcium fluoride was without observable detrimental effect upon germination or upon sequential seedlings; did not promote plant growth; was not adequate as a source of nutrient calcium; and was of nugatory value as a liming material. Incorporated alone at heavy rates, calcium fluoride increased materially the fluorine concentration in the tops of two nonlegumes, whereas simultaneously incorporated supplements of superphosphate induced a decided diminution in the fluorine content of rye grass. Alfalfa growth was induced by the calcium from the 2-ton incorporations of limestone, and of slag, whereas such growth was not induced by the Ca supplied by the equivalent inputs of fluoride.

The fluoride caused some percentage increase of fluorine in the tops of alfalfa, the roots of which showed fluorine enrichment beyond that found for its tops,

whereas the tops had a higher content of  $P_2O_5$ . It is believed that probable input of fertilizer-component calcium fluoride would not exert any harmful effect upon plant growth and composition. Although the present experimental findings demonstrate absence of detrimental effect from incorporations of calcium fluoride equivalent to rational limings, the findings do not warrant the conclusion that the fluorides carried by incorporations of phosphatic fertilizers are of no benefit in the soil system.

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# BASE-EXCHANGE EQUILIBRIUMS IN SOILS AND OTHER EXCHANGE MATERIALS<sup>1</sup>

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In recent years the use of ion exchange materials in research and industry has increased continually. Their use to remove either cations or anions from solutions, particularly for water softening and for solution purification, is an accepted procedure. Soil chemists have long recognized that many chemical and physical properties of soils are directly related to their exchange properties. Thus the prevention of the loss of plant nutrients by leaching is largely controlled by the exchange properties of the soil. The so-called available plant nutrients, especially the cations, are those held on the exchange surface of the soil colloid and released through exchange phenomena to the root surface or soil solution. Though the existence of base-exchange phenomena and their effects on a given system have been demonstrated, the actual dynamics of exchange adsorption are not well understood. Investigators are not agreed as to whether exchange reactions follow the law of mass action, laws of adsorption, or the Donnan equilibrium. It was, therefore, the purpose of this investigation to study some of the factors, such as concentration, ratio of ions, and exchange materials, which might affect base-exchange reactions.

## LITERATURE REVIEW

The ionic exchange phenomenon was first observed by Way (27) in 1850 when he passed a solution of potassium chloride through a bed of soil and found that a quantity of sodium and calcium, equal to the quantity of potassium adsorbed, was released from the soil. Since that time many colloidal systems like proteins, soap, hydrous oxides, aluminosilicates, and resins have been found to exhibit the phenomenon of ion exchange.

The earliest students of ionic exchange attempted to apply established adsorption equations like that of Freundlich or Langmuir to exchange data. These attempts were not too successful. In 1913 Gans (6) applied the law of mass action to exchange adsorption and derived the following equation:

$$K = \frac{X^2}{(m \cdot n - X)(g - X)}$$

where  $K$  = equilibrium constant,  $n$  = total amount of exchangeable bases in the exchange complex,  $m$  = exchange complex in grams,  $g$  = total amount of salt in solution, and  $X$  = amount adsorbed. The mass action law was again applied by Rothmund and Kornfeld (22) in 1918. The relation  $\left(\frac{C_1}{C_2}\right)_{\text{solid}} = K \left(\frac{C_1}{C_2}\right)_{\text{solution}}$  was suggested, in which  $C_1$  and  $C_2$  are the concentrations of ions 1 and 2.

Wiegner and Jenny (29) then suggested the relationship involving amounts of ion present,

<sup>1</sup> Contribution from the department of agronomy, Agricultural Experiment Station University of Illinois. Published with approval of the director.

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thus  $y = K \left( \frac{c}{a - c} \right)^p$ , where  $y$  = amount of exchange per gram solid,  $K$  = constant,  $c$  = concentration (equivalents) of added ion after equilibrium,  $a$  = concentration (equivalents) of added ion before equilibrium,  $p$  = constant less than one. Later Vageler (24, 25) suggested an equation similar in form to Langmuir's adsorption isotherm:  $y = \frac{as}{a + c}$ , where  $y$  = amount adsorbed per gram adsorbing substance,  $a$  = amount of salt (equivalents) added per gram of adsorbing substance,  $s$  = maximum exchange capacity of solid,  $c$  = constant but represents the concentration of  $a$  at which 50 per cent of  $s$  is exchanged.

The equation suggested by Kerr (15) is identical with the one suggested by Gans (6). In 1932 Vanselow (26) attempted to apply the law of mass action to base-exchange equilibria. Working with dilute solutions he found the law of mass action applicable to some systems and suggested hysteresis as being responsible for its failure in others.

Jenny (11) suggested an equation which is not empirical in nature and which is supposedly not based on the law of mass action. Using simple kinetic theories and the Poisson series, he arrives at the following equations:

$$W = \frac{+(s + N) \pm \sqrt{(s + N)^2 - 4sN(1 - V_w/V_b)}}{2(1 - V_w/V_b)}$$

where  $W$  = number of cations adsorbed or released at equilibrium of species  $w$ ,  $N$  = amount of electrolyte added initially (number of ions),  $s$  = saturation capacity of exchanger,  $V_w$  = oscillation volume of ions of type  $w$ ,  $V_b$  = oscillation volume of ions of type  $b$ .

Jenny's equation may, however, be derived on the basis of mass action. If an exchange reaction is illustrated by the following equation,  $KX + NaCl \rightleftharpoons NaX + KCl$ , where  $X$  = colloid, then, since only two ions are involved,  $W$  ions of potassium will have been released and  $W$  ions of sodium clay formed at equilibrium. Written in mass action form, the equation becomes

$$K = \frac{W^2}{(N - W)(s - W)} \quad \text{or} \quad W = \frac{+(s + N) \pm \sqrt{(s + N)^2 - 4sN(1 - 1/K)}}{2(1 - 1/K)}$$

then  $1/K = V_w/V_b$ , and  $K = V_b/V_w$ ; or stated in another way, the ratio of the oscillation volume, for the reacting ions, expressed in Jenny's equation is an expression of the mass action equilibrium constant for the reaction involved.

Giesecking and Jenny (7), studying the behavior of monovalent and polyvalent cations in base-exchange reactions with Putman clay, concluded that although the behavior of the ions is irregular, it appeared that the electric charge and the size of the ions were the two major factors which determine the position of an ion in adsorption and release. For clays saturated with monovalent and polyvalent cations the adsorption of monovalent cations yields the lyotropic series, namely  $Li \leq K < NH_4 < Rb < Cs < H$ . Unlike the monovalent cations, the divalent cations formed a different series, depending upon the ion on the colloid. Thus  $NH_4$ -clay gave the series  $Mg \leq Ca < Sr < Ba$ ;  $H$ -clay gave the series  $Mg < Ba < Ca < Sr$ ; and  $Ca$ -clay gave the series  $Mg < Ca < Ba$ . Later Giesecking (8) worked with larger complexions like piperidine, brucine, aniline, and methylene blue and found that these larger cations were very strongly adsorbed. He also found that once these larger ions were adsorbed they were not replaced by small ions like hydrogen but were replaced by ions of approximately the same size.

Jenny and Overstreet (12, 13), in a study of contact exchange between the plant root-hairs and clay particles, found that ions were apparently able to diffuse or migrate along the colloid surface and to move from one particle to another when the particles were in contact with each other. Using radioactive sodium they found that more sodium was adsorbed by barley roots from a  $Na$ -clay than from a solution containing an equal amount of sodium as either the chloride or the bicarbonate.

Clarens and Lacroix (4) studied the displacement of calcium by potassium. They represent the calcium clay as clay- $\text{Ca}_1, \text{Ca}_2, \text{Ca}_3, \dots, \text{Ca}_n$ , the index marking the order of displacement. On this basis they postulated the following formula for replacement:

$dY/dX = K(A - Y)$ , which integrated gives  $\log(A - Y) = -KX + C$  where  $A$  = base-exchange capacity,  $Y = \text{Ca}$  replaced,  $X$  = potassium added, and  $C$  and  $K$  = constants.

Ivanov and Gapon (10) consider ion exchange to be dependent upon the dilution of the solution used. Their theory, based on exchange between silicates and electrolyte solutions suggests that the amount of adsorbed cations is independent of the dilution of the equilibrium solution if the exchange ions have the same valence. If the ions are of different valences, dilution of the equilibrium solution increases the adsorption of the ion of greater valence. On this basis they formulate the following exchange equation:

$$S_1 = \alpha_1^0 + \omega \log(A_1^{1/N_1}/A_2^{1/N_2})$$

where  $S_1$  is the adsorbed ion,  $A_1$  and  $A_2$  are ion activities, and  $N_1$  and  $N_2$  are the valences.

Walton (28) made a rather complete study of the field of ion exchange, and in his discussion he said, "In the experience of the writer, the equation of Rothmund and Kornfeld is as generally satisfactory as any in expressing ion exchange distribution." In applying the equation of Rothmund and Kornfeld to large numbers of published exchange data, Walton found that the higher the atomic weight of the ion, the more firmly it is held by the exchanger; and in general he established the lyotropic series for the cations. He found that for a constant concentration the monovalent ions, with the exception of hydrogen, are held less tightly than the divalent ions, and the divalent cations less tightly than the trivalent ions. With respect to the ratio of ions Walton found that in exchange between ions of equal valence, the ratio of the concentration of the ions in the exchanger depends only on the ratio of their respective concentrations in solution, not on the total concentration of the solution. In exchanges between ions of different valence the proportion of the ion of higher valence in the exchanger is greater, the more dilute the solution.

In all the work reviewed so far, the investigators have limited themselves to systems of two ions. The equations established have been restricted to systems of two ions and, therefore, have had only limited application in the practical field. The first attempt to formulate a working base-exchange equation for systems of more than two ions is found in the work of Bray (3). In formulating his equation, Bray said: "It can be assumed that the ratio of a given cation to the total cations released when a small amount of electrolyte is added, is proportional to (1) the relative amount present in the exchangeable form and (2) the relative ease of release." He expresses this mathematically as follows:

$$K_p = \frac{Kf_k}{Kf_k + \text{Ca}f_{ca} + \text{Mg}f_{mg} + \text{H}f_h}$$

where  $K_p$  = ratio of potassium released to the total cations released from the colloid, where the release is small compared to the cation-exchange capacity; K, Ca, Mg, H, are the exchangeable cations; and  $f_k, f_{ca}, f_{mg}, f_h$ , are constants for "relative" ease of release for the respective cations. With this as a working basis, Bray developed six equations by which it is possible to calculate the equilibrium of any system of mixed ions. Any calculation requires the use of three equations which fit the proper conditions. As a result of the reactions represented by his equations, Bray (3) set up the following seven rules which express the relationship governing exchange competition:

1. Where a cation of a higher  $f$  (ease of release) value is replaced from the colloid by one with a lower  $f$  value, the proportionate release of the other ions present on the colloid will be increased.
2. Where a cation of a lower  $f$  value is replaced by one with a higher  $f$  value, the proportionate release of the other cations present on the colloid will be decreased.



3. The higher the average  $f$  value for the cations on the colloid as a whole, the greater the buffering ability, *i.e.*, the greater is the adsorption of an added cation.
4. Substituting a cation of a higher  $f$  value for one with a lower  $f$  value in the electrolyte increases the adsorption of the accompanying electrolyte cations.
5. Substituting a cation of a lower  $f$  value for one with a higher  $f$  value in the electrolyte decreases the adsorption of the accompanying electrolyte cations.
6. The higher the average  $f$  value for the electrolyte added, the less is its replacing ability.
7. The smaller the amount of electrolyte added, the greater is the relative influence of the "ease of release" or  $f$  value on the amount of a given cation released.

Magstad, Fireman, and Mabry (16) in a comparison of base-exchange equations found that the equations of Kerr, Vanselow, and Gapon, which are all based on the mass action principle, were more satisfactory than equations based on adsorption theories. Davis (5), however, found that the Donnan equilibrium more nearly expressed the base-exchange equilibrium reaction than did either mass action equations or the adsorption type of equations. The diversity of findings and views in the foregoing review is evidence of the uncertainty of present knowledge of the dynamics if not the mechanism of the cation-exchange process.

#### MATERIALS AND METHODS

The exchange materials used in this study are natural silicates and synthetic exchangers. The soil samples are a part of a former soil study. Soil 14037 is the B horizon of Hartsburg silt loam, composed largely of illite-beidellite clay minerals with a base-exchange capacity of 28 m.e. Soil 16617 is the B horizon of Cisne silt loam, composed largely of montmorillonite-beidellite clay minerals with a base-exchange capacity of 26 m.e. The Kentucky ball clay is a sample of kaolin from Graves County, Kentucky, with an exchange capacity of 15 m.e. per 100 gm. The Pennsylvanian shale is a sample of the underclay from Menard County, Illinois, with an exchange capacity of 9.8 m.e. per 100 gm.; it is almost pure illite. Amberlite IR-1, Permutit, and Zeo-Karb are the standard commercial products furnished under those names.

The analytical methods used are standard methods in common use (2). The soils are leached with neutral ammonium acetate, washed with alcohol, then leached with acid, and the ammonia released is determined. The acetate leachate is then taken to dryness, ignited, the residue dissolved in excess of standard HCl and back-titrated for total exchangeable bases. For exchangeable calcium and magnesium the latter solution is taken to dryness, and silica and sesquioxides are removed. Ca is precipitated as oxalate and titrated either with  $\text{KMnO}_4$  or with hexa nitrate ammonium cerate, nitro-orthophenanthroline being used as indicator. Magnesium is determined in the Ca filtrate gravimetrically either as  $\text{Mg}_2\text{P}_2\text{O}_7$  or  $\text{Mg}(\text{C}_2\text{H}_3\text{NO})_2$ . Potassium is determined volumetrically by titration of the potassium sodium cobaltinitrite precipitate, proper precautions being used as to temperature and both a standard K solution and a blank being carried along with each set.

The term "symmetry value" as used here expresses the condition in which the number of milliequivalents of exchangeable cations on the colloid is equal to the total milliequivalents of salt in solution.

## EXPERIMENTAL

*Equilibrium systems*

For the natural silicates, 5 gm. of the calcium-saturated material was shaken with one symmetry of salt in 50 ml. of water. For the higher exchange materials 2-gm. samples were used. The equilibrium period was 48 hours, the equilibrium mixture being shaken on a mechanical shaker  $\frac{1}{2}$  hour every 12 hours. The temperature varied from 22° to 25° C. After equilibrium was reached, the materials were allowed to settle and the supernatant liquid was decanted and filtered. The calcium released to the solution was determined on an aliquot of the filtrate. In all cases the chloride anion was used. Redistilled water was used to make up all the solutions.

The first object was to determine the relative accuracy of the published  $f$  values of Bray. It was decided that this would best be accomplished by using calcium-saturated exchange material and adding one symmetry of a single

TABLE 1

*Percentage of adsorbed calcium released from a calcium-saturated material on addition of one symmetry of salt, and the calculated  $f$  values for various ions*

	NaCl		KCl		MgCl <sub>2</sub>		HCl	
	Ca released	$f$	Ca released	$f$	Ca released	$f$	Ca released	$f$
	per cent		per cent		per cent		per cent	
Soil 14037 electrodyalyzed.....	15.7	5.4	33.7	2.0	44.8	1.2	70.2	0.42
Soil 16617 electrodyalyzed.....	15.2	5.6	36.6	1.7	46.6	1.1	70.8	0.41
Kentucky ball clay electrodyalyzed..	14.4	5.9	36.5	1.7	45.0	1.2	68.9	0.45
Pennsylvanian shale electrodyalyzed	15.9	5.2	36.8	1.7	47.0	1.1	71.5	0.40
Amberlite IR-1 electrodyalyzed.....	15.9	5.2	23.3	3.3	40.4	1.5	48.5	1.05

salt, thus allowing for the free competition of the two ions on the colloid. The  $f$  value would then be calculated by dividing the percentage saturation of calcium by the percentage saturation of the complementary ion. The results are given in table 1. In general, the  $f$  values obtained are slightly lower than those obtained by Bray—2.2, 1.6, 1.0, and 0.35 for K, Mg, Ca, and H respectively—but they are in excellent agreement among themselves. It is particularly interesting to note that the two soils and the natural silicates are in almost perfect agreement, whereas Amberlite, a synthetic resin, has a different set of  $f$  values.

The next point considered was the effect of dilution of the equilibrium solution on the final distribution of the ions on the exchange surface. A system of ions of equal valence was first investigated. Table 2 gives the results when one symmetry of salt was added in 50 ml. and in 2,000 ml. of water. A slight change was observed in the proportion of the cations adsorbed by the colloid for both the monovalent and the divalent systems. As a solution of ions of the same valence was made more concentrated, the ion with the lower  $f$  value increased on the colloid. Systems of ions of different valences—Ca-K, NH<sub>4</sub>-Ca, and K-Mg—

were next investigated. As shown in table 3 for the Ca-K system, which was chosen to illustrate the trend, the ion of lower valence decreased on the colloid as the solution was made more dilute.

The ratio at which ions accumulate on the surface of an exchange material depends on three main factors; namely, (a) the concentration of the solution, (b) the nature of the exchange material, and (c) the nature of the ions competing for the exchange surface. The effect of the soluble anion may be a factor, inasmuch as it may influence one cation more than another if the solution is very concentrated. If the two cations associated with the anion have approximately the same solubility, the anion effect should be small.

TABLE 2

*Distribution of the cations on soil 16617 as affected by the dilution of a solution of ions of the same valence*

VOLUME	Ca-Mg SYSTEM			K-Na SYSTEM		
	Distribution on colloid			Distribution on colloid		
	Ca	Mg	Mg/Ca	K	Na	K/Na
ml.	m.e./100	m.e./100		m.e./100	m.e./100	
50	14.2	13.5	0.95	18.5	8.0	2.3
2,000	12.5	14.0	1.12	18.7	7.5	2.5

TABLE 3

*Distribution of the cations on soil 16617 as affected by the concentration of a solution of cations of different valences*

VOLUME	Ca-K SYSTEM		
	Distribution on the colloid		
	Ca	K	K/Ca
ml.	m.e./100	m.e./100	
50	15.3	9.1	0.59
2,000	17.2	5.2	0.30

The  $f$  value of Bray and the "oscillation volume" of Jenny attempt to show the relative ease of release or tightness of retention with which cations are held on the exchange surface. Thus an ion having a high  $f$  value or a large "oscillation volume" will be more easily replaced than an ion with a small  $f$  value or a small "oscillation volume." The  $f$  value is based on the condition that the displacing solution is dilute and also on the condition that the total amount of ions released from a colloid by a displacing solution is small in proportion to the total amount of these ions held on the colloid. Let us assume that we have a colloid containing 0.1 m.e. of K and 9.9 m.e. of Ca and that enough 0.05  $N$  HCl is added to displace 1 m.e. of total bases. Under this condition the release is small compared to the total bases present, and the ratio of the two cations released will be determined by the ease of release of the individual cations and the

amount of each present. Now assume that conditions are changed so that enough HCl is added to displace 9.9 m.e. of total bases. Under this condition virtually all of the bases are released so that the composition of the base mixture released is not governed by the relative ease of release of the Ca and K but by the amount of these cations present on the colloid. That is, practically 100 per cent of both cations is released and therefore the observed  $f$  values of both Ca and K would be unity. For the latter condition two views may be taken: (a) that the  $f$  values change as one goes from a small amount of release to complete release and therefore approach 1 for all ions, or (b) that free competition does not exist under this condition but that it exists only when the amount of any one cation in the equilibrium system is not sufficient to dominate completely the exchange surface of the colloid.

The data in table 1 have shown the general nature of the cations competing for a position on the exchange surface of a natural silicate when in a chloride solution. These values were obtained in a closed system, that is, all of the cations in the system were capable of exerting their composite force on the final equilibrium. Here, then, are the basic components for establishing an equilibrium exchange equation for any number of cations; namely, (a) the relative ease with which a cation is held or released, (b) the effect of mass or amount of the cation present, and (c) the knowledge that we are working with a closed system and must, therefore, consider the total of all of the ions that make up the system. Expressed mathematically this would give:

$$A_0 = \left( \frac{A \cdot f_a}{A \cdot f_a + B \cdot f_b + C \cdot f_c + \dots + N \cdot f_n} \right) \times \text{m. e. of anion},$$

where  $A_0$  = milliequivalents of ion  $A$  in solution after equilibrium;  $A, B, C, N$  = total milliequivalents of each of these cations in the system;  $f_a, f_b, f_c, f_n$  = the respective  $f$  values for the ions  $A, B, C, \dots, N$ . Or, if it is desirable to express the distribution of the ions on the colloid, the equation takes the same form except that the reciprocal of the  $f$  value is used, that is, the ease of retention of the cation.

$$f_1 = \left( \frac{A \cdot 1/f_a}{A \cdot 1/f_a + B \cdot 1/f_b + C \cdot 1/f_c + \dots + N \cdot 1/f_n} \right) \times \text{m. e. exchange capacity},$$

where  $A_1$  is the milliequivalents of cation  $A$  on the colloid. This simple equilibrium equation has been applied to a larger number of published exchange data of various workers and was found to hold over a wide range of soils and concentrations. This equation may also be derived mathematically by combining two equations suggested by Bray (3); namely, his equation for total release (equation 13) and his equation for single ion release (equation 1).

### *Leaching systems*

For the leaching studies where four cations were used in the leaching solution, 10-gm. samples of the natural silicates were leached under suction with 1,500 ml. of solution (10,000 ml. were used for the 0.005  $N$  solution). Smaller samples

of the higher exchange materials were used. After leaching, the materials were washed with neutral methyl alcohol, then leached with neutral normal ammonium acetate, the latter leachate was evaporated, ignited, and the total bases as well as each of the individual bases were directly determined. Hydrogen was determined by difference between the total bases and the exchange capacity of the colloid. In all cases the colloid was saturated with ammonium before the initial leaching with the cation mixture. For all two-cation leaching systems only the total bases and one cation were determined. The second cation was determined by difference. Except for the study of the effect of the anion on the cation distribution on the colloid, the chloride anion was used in all leaching solutions.

It was seen from the equilibrium studies that cations differ significantly in their ease of release or retention. It would therefore be expected that if an exchange material were leached with a dilute solution of cations in equal ratios, the final distribution of these ions on the colloid would be in an inverse relation.

TABLE 4

*Distribution of the cations on various exchange materials as affected by the concentration of a four-ion leaching solution*

	SOIL 14037				SOIL 15617				PENNSYLVANIAN SHALE				KENTUCKY BALL CLAY				AMBERLITE	
	0.005 <i>N</i>	0.05 <i>N</i>	0.25 <i>N</i>	1.0 <i>N</i>	0.005 <i>N</i>	0.05 <i>N</i>	0.25 <i>N</i>	1.0 <i>N</i>	0.005 <i>N</i>	0.05 <i>N</i>	0.25 <i>N</i>	1.0 <i>N</i>	0.005 <i>N</i>	0.05 <i>N</i>	0.25 <i>N</i>	1.0 <i>N</i>	0.05 <i>N</i>	0.25 <i>N</i>
	m.e.*	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.	m.e.
Ca.....	6.62	5.26	3.38	2.32	5.28	5.00	2.88	1.84	1.65	1.80	1.20	0.68	3.64	3.04	1.51	0.60	4.0	32.5
Mg.....	5.31	4.35	2.56	1.63	4.18	4.12	2.36	1.79	1.49	1.82	1.15	0.64	2.92	2.68	1.41	0.77	20.0	17.0
K.....	2.06	4.44	9.06	11.70	2.00	4.40	7.48	10.74	0.79	0.70	2.36	3.36	2.12	2.94	6.12	7.62	8.0	15.0
H.....	14.01	13.95	13.00	12.05	14.64	12.48	13.30	11.63	5.67	5.48	5.09	5.12	6.32	6.34	5.96	6.01	83.0	85.0
Total bases...	13.99	14.05	15.00	15.95	11.36	13.52	12.70	14.37	4.13	4.32	4.71	4.68	8.68	8.66	9.04	8.99	62.0	64.5

\* m.e. = milliequivalents per 100 gm.

to their *f* values. To test this theory, four-ion solutions of K, Mg, Ca, and H in a 1:1:1:1 equivalent ratio at 0.005 *N*, 0.05 *N*, 0.25 *N*, and 1.0 *N* were prepared and several exchange materials leached with them. Since the *f* values were 1.7, 1.2, 1.0, and 0.41 for K, Mg, Ca, and H respectively, it was expected that on the colloid the order of decreasing magnitude would be H, Ca, Mg, and K. The results obtained are given in table 4. The 0.05 *N* solution is of the same approximate normality as the one symmetry equilibrium solutions.

The data in table 4 are exceedingly interesting and of considerable value. Four points should be particularly noted: (a) the predicted order of magnitude of the ions on the exchange surface held only in the extremely dilute range of leaching solution, (b) the relative ratio of Ca to Mg was the same on all silicate materials and changed little with concentration, whereas the ratio of K to the divalent cations reversed itself with increasing concentrations, (c) the amount of H on the colloid was almost constant at all concentrations but tended to decrease with increasing concentration of the leaching solution, and (d) the four

natural silicates behaved similarly as a group, but Amberlite behaved differently from them. Obviously, it is impossible to predict the distribution of the cations on the exchange surface in a leaching system from the  $f$  values obtained in the equilibrium systems.

It was observed in the earlier work that the type of exchange materials had a marked effect on the distribution of the cations on the exchange surface and on the effect resulting from changes in the concentration of the leaching solution. This point was further investigated by leaching several types of exchange materials with leaching solutions containing 1:1 ratios of cations of the same valence. The data are reported in figures 1 and 2. In these graphs the percentage of the exchange surface occupied by one cation is plotted against the log of the total

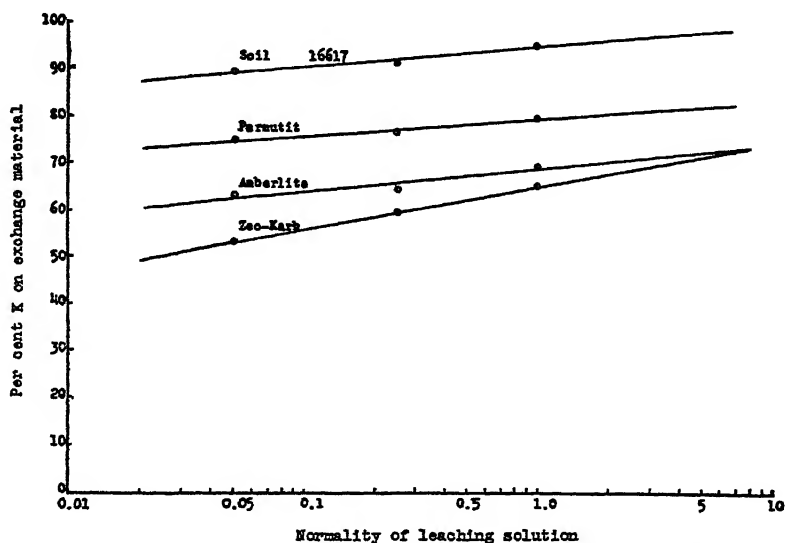


FIG. 1. CHANGE IN PERCENTAGE K ON EXCHANGE SURFACE WITH CHANGE IN CONCENTRATION OF A 1:1 K-Na LEACHING SOLUTION

concentration of the leaching solution. It is interesting to note that for the monovalent cations the K/Na ratio on the colloids ranges from approximately 1.1 for Zeo-Karb to about 8.2 for the soil although the concentration remains constant at 0.05  $N$ . It is likewise observed that in all cases the K/Na ratio increases with increasing concentration of the leaching solution. In the case of the divalent cations, Mg and Ca, the situation is quite different. Again a marked variation in the Mg/Ca ratio is observed for different exchange materials at any given concentration of leaching solution. For the natural silicates and Permutit the Mg/Ca ratio increases, whereas for Amberlite and Zeo-Karb it decreases with increasing concentration of the leaching solution. Apparently it is not possible to predict the trend of the Mg/Ca ratio with changes in concentration unless the nature of the exchange material is known.

For leaching solutions containing cations of different valence the effect of the

exchange material is even more striking. Figure 3 gives the data obtained on leaching several exchange materials with 1:1 Ca-K chloride solutions at dif-

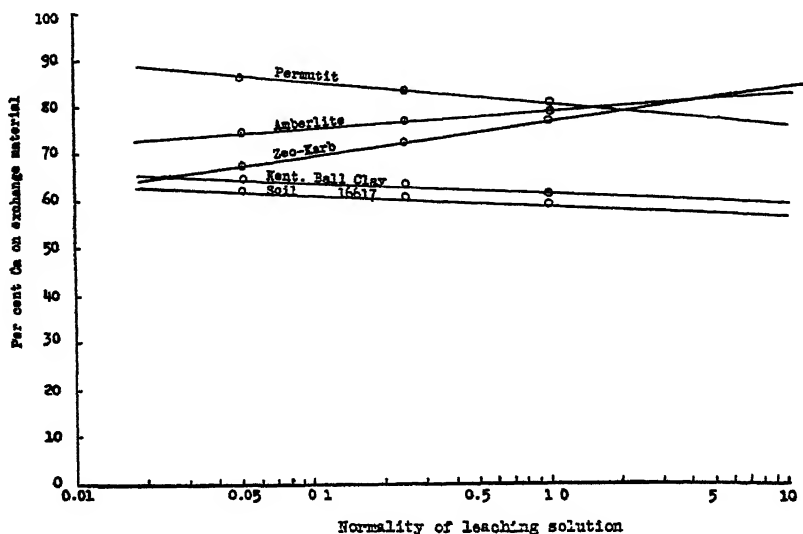


FIG. 2. CHANGE IN PERCENT Ca ON EXCHANGE SURFACE WITH CHANGE IN CONCENTRATION OF A 1:1 Ca-Mg LEACHING SOLUTION

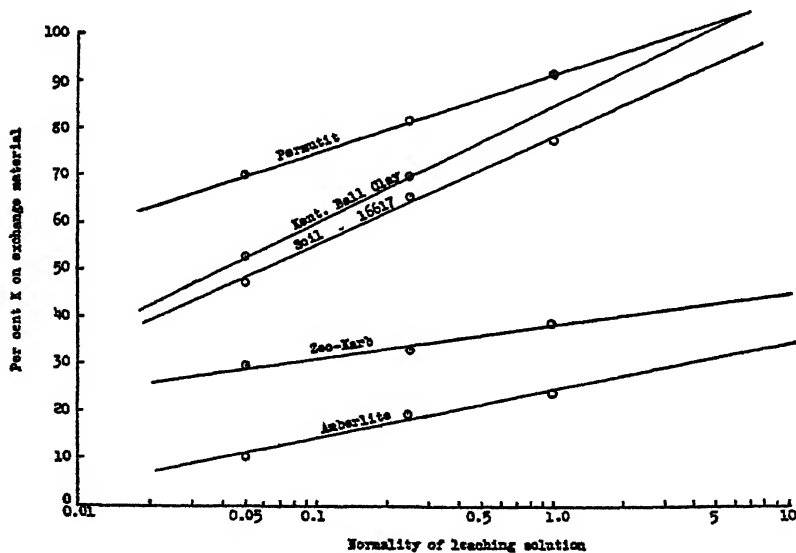


FIG. 3. VARIATION IN PERCENTAGE K ON COLLOID WITH CHANGING CONCENTRATION OF A 1:1 K-Ca LEACHING SOLUTION

ferent concentrations. Here the K/Ca ratio on the colloid varies from approximately 0.1 for Amberlite to approximately 2.4 for Permutit at 0.05 N concen-

tration. In other words, the Amberlite preferentially adsorbs calcium, whereas Permutit adsorbs potassium.

In one respect all of the exchange materials were consistent, the K/Ca ratio always increased with increasing concentration of the leaching solution. However, the nature of the exchange material will determine which cation will predominate on the exchange surface.

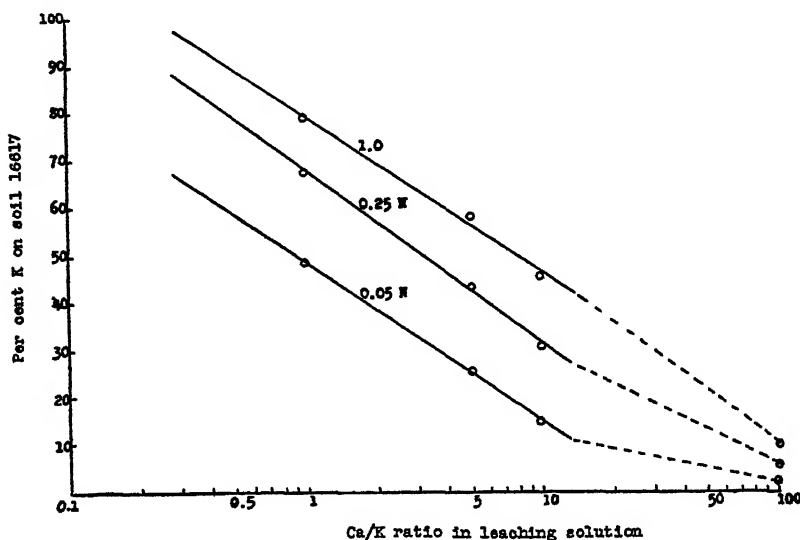


FIG. 4. CHANGES IN PERCENTAGE K ON SOIL 16617 WITH CHANGES IN THE Ca:K RATIO IN THE LEACHING SOLUTIONS AT DIFFERENT NORMALITIES

TABLE 5

*Distribution of cations on soil 16617 as affected by the concentration and by the associated anion of a 1/1 Ca-K leaching solution*

ANION	DISTRIBUTION OF IONS ON COLLOIDS								
	0.05 N			0.25 N			1.0 N		
	Ca	K	K/Ca	Ca	K	K/Ca	Ca	K	K/Ca
	m.s./100	m.s./100		m.s./100	m.s./100		m.s./100	m.s./100	
Chloride.....	11.2	10.0	0.89	7.2	14.3	1.98	5.1	17.5	3.44
Nitrate.....	10.1	10.2	1.02	7.0	13.7	1.95	5.2	15.8	3.05
Sulfate.....	7.7	8.9	1.15	....	....	....	....	....	....
Acetate.....	10.8	10.5	0.97	7.3	14.2	1.94	5.1	16.7	3.27

It has been shown how the cations behave with changes in concentration of the leaching solution. The effect of the ratio of the ions at constant total concentration can now be considered. For this purpose the data on soil 16617 and the Ca-K chloride leaching solutions are presented. Figure 4 shows the results obtained when soil 16617 was leached with solutions of varying concentrations and ratios of Ca-K. The ratios were so chosen that, as they widened, the monovalent



cation would decrease in concentration while the divalent cation would increase, the over-all concentration of the leaching solution remaining constant. This was necessary in order to prevent the monovalent cation from completely dominating the exchange surface. It will be observed that as the proportion of K with respect to Ca in solution decreased, its proportionate retention on the colloid decreased much more slowly. As seen in figure 4, the percentage of K on the exchange surface changed as the log of the ratio of the cations in solution.

The type of exchange material has been shown to be a significant factor in determining the distribution of the cations on the exchange surface. What then is the effect of the anion, associated with the cations in solution, on the final distribution of the cations on the exchange surface? To evaluate this factor ammonium-saturated soil 16617 was leached with three concentrations of 1:1 Ca-K leaching solutions in which different anions were used. The data are presented in table 5. In general, the anion had no significant effect on the final distribution, that is, on the K/Ca ratio on the exchange surface. The anion had an effect on the total amount of the cations adsorbed, but this effect was small until the solution approached saturation.

#### DISCUSSION

The purpose of base-exchange studies is twofold; namely, (a) to determine the factors that may influence the exchange reactions and their relative significance, and (b) to attempt to express these factors mathematically for practical application. The leaching systems, like the equilibrium systems, are influenced by four main factors: (a) concentration of the leaching solution, (b) type of exchange material, (c) nature of the cations, including their valence, activity or  $f$  value, and size, and (d) ratio of the ions in solution. An attempt to evaluate these factors for the leaching systems and express them mathematically has been made by Melsted (17), who assumed (a) that the distribution of the ions on the colloid represents the true equilibrium condition between the exchange material and the leaching solution, and (b) that the  $f$  values obtained for the equilibrium system represents the true relationship between the cations in a leaching solution at infinite dilution.

The data presented here in figures 1, 2, and 3 may be expressed mathematically in the form of equations for the straight lines for each of the exchange materials. Thus for the Ca-K system one might express the data as follows:

$$\text{for soil 16617} \quad y - 27 \log x = 80$$

$$\text{Amberlite} \quad y - 10 \log x = 24$$

$$\text{Zeo-Karb} \quad y - 7 \log x = 38$$

$$\text{Permutit} \quad y - 17 \log x = 92$$

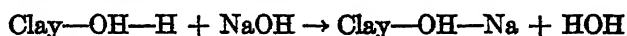
where  $y$  = percentage K on the colloid,  $x$  = total concentration of the 1:1 Ca:K leaching solution. It was observed from figure 4 that the percentage K

on the colloid for any given concentration varied as the log of the Ca/K ratio. This may be incorporated into the above equations so that, for soil 16617 as an example, one would get the following equation:  $y - 27 \log x = 80 - 31 \log r$ , where  $r$  is the Ca/K ratio.

It might be assumed from the data that it would be possible so to choose the ratio of cations and the concentrations of the solutions that the adsorption of one cation would be completely prevented. When tested in both extremes of concentration it was found that in a 1:1 Ca:K system it was not possible completely to dominate the exchange surface with either ion. When the ratio of the ions was varied so that the concentration of any one ion became extremely dilute, the volume of leachate used became such a significant factor that no definite conclusions could be drawn from the experiments.

The place of hydrogen in a leaching system is the most difficult to evaluate. A very small amount of hydrogen seems to be highly effective in preventing the accumulation of other ions. There seems to be no direct relationship between the concentration of the H ion in solution and its accumulation on the colloid. The H ion does not appear to accumulate on the colloid with increasing concentration, as do both K and Na between 0.005 *N* and 1.0 *N*. When hydrogen is present with either K or Na in a leaching solution, it actually decreases on the colloid with increasing concentration of the leaching solution.

It has been amply demonstrated that the type of exchange material used will largely determine the relative distribution of the ions on its exchange surface. An explanation for the differences exhibited by the exchange materials is suggested in the work of Johnson and Norton (14). These investigators represent the base-exchange reaction as follows:



and then say, "The reaction will proceed to the right because of the establishment of a system with a lower free energy." If it is assumed that exchange reactions are true energy equilibria and that the  $f$  values represent the relative energy levels of the ions, it may be concluded that the percentage distribution of the cations on the exchange material in a leaching system is controlled by the relative energy level of the exchange material. In the leaching system the energy level of the leaching solution remains almost constant, and therefore the distribution of the ions on the colloid varies as the energy levels of the exchange materials differ. Thus an exchange material with a high energy level will adsorb more of the ions of lower energy while an exchange material with a low energy level would require more of the ions of high energy in order to establish an equilibrium with the same leaching solution. Such a theory would account for the experimental fact that the anion associated with the cations in the leaching solution has a very small effect on the ratio of the ions on the exchange surface but does effect the total amount of bases adsorbed. On the basis of such an energy concept, it would be concluded that Permutit, with its high adsorption for K, has a much higher energy level than Amberlite, which has a high preferential adsorption for calcium.

## GENERAL APPLICATIONS

A detailed knowledge of the equilibriums existing between the exchangeable cations on the soil and the soil solution is essential for an understanding of the problems of soil fertility and plant nutrition. It has been known for some time that the so-called available cations of the soil are those held on the colloidal clay exchange surface and released to the plant roots and soil solution through exchange equilibriums. But just knowing that the available ions are held on the exchange complex is not sufficient; we must know how they act in relation to soil fertility practices. This study has indicated some very interesting applications in this respect.

The most common cation added to the soil for its plant-food value is potassium. Many agronomists in the central and coastal plain states have been concerned over the probable loss of this element through leaching, their contention being that since the element is added as a soluble fertilizer it would quickly leach through the root-feeding zone of the soil. The data presented here have indicated that potassium retention on the colloid increases with concentration. Thus a concentrated fertilizer application of potassium is actually more favorable to its retention than is a more conservative application. In this connection it is of interest to point out that recently large applications of potash were applied to some of the Illinois lysimeters and resulted in large increases of calcium and magnesium but no relative increase of potassium in the drainage water. This is in accordance with expectations based on the foregoing equilibrium studies.

The equilibrium data further support the observation of Bray (3) that liming on acid soil will decrease the relative amount of potassium that will be released by any given electrolyte. Therefore, a practical soil-improvement program should include the use of soluble potash fertilizers in any liming program, if the soil is on the border line of potassium deficiency, in order to prevent the occurrence of such deficiencies.

A further application of equilibrium data is found in the field of plant nutrition. Plant physiologists are often concerned with "active" or "physiological" adsorption, which Miller (18) defines as the "the absorption of solutes by cells after a manner contrary to the ordinary laws of diffusion." As an example of this type of absorption the *Valonia* and *Nitella* are most frequently cited. It is pointed out that the concentration of potassium is forty times as great in the cell sap of *Valonia* as it was in the original sea water, while the concentration of sodium is one fourth or one fifth as great. Yet this is only what would be expected from equilibrium studies. Plant roots have been shown to exhibit exchange properties (12, 13), and it may be assumed that the surface of *Valonia* exhibits the same property. Also exchange surfaces have been shown to accumulate twenty times as much potassium as sodium (see soil 16617, fig. 2) from a solution containing equal amounts of these ions. Sea water usually contains twenty times as much sodium as potassium; therefore, the *Valonia* exchange surface need only be similar in character to that of a soil in order that sodium and potassium accumulate in a 1:1 ratio on its exchange surface. This being the

case, ordinary laws of diffusion could readily explain the greater amount of potassium in the cell sap. It is the distribution of the ions on the adsorbing surface that predominates over the distribution of the ions in solution, when plant absorption is considered.

Equilibrium studies in plant growth may be of considerable importance. In this connection the work of Itallie (9) on cation equilibria in plants is of interest. He shows what effect the presence of the ions Ca, Mg, Na, and K in various combinations has on the absorption of any one ion. He establishes a series of relationships for the correlation of the nutrient level in the soil with uptake by the plant. The relation for potassium is taken for an example:

$$K = \frac{20K}{0.1 \text{ Ca} + 0.2 \text{ Mg} + \text{Na}}$$

where K, Ca, Mg, and Na = amounts of these ions in the soil. It is not improbable that a direct equilibrium may be found to exist between the cations in the soil and the cations absorbed by plants.

Exchange materials, such as Permutit and various types of zeolites, have been used industrially for many years as water-softening agents. Lately Amberlite has received considerable publicity (19, 20, 21) as an exchange material supposedly far superior to other exchange materials. That Amberlite is an excellent exchanger for water softening is confirmed by the leaching equilibrium data presented here. It has a very high affinity for calcium and will therefore adsorb that ion from solution much more readily than will an exchange material like Permutit, which preferentially adsorbs potassium. But although Amberlite has good qualities as a water softener, it does not have superior exchange qualities for all purposes. For adsorbing an ion like potassium from a solution, Permutit would be far superior to Amberlite.

The concentration of rare metals or ions from dilute industrial wastes (1) through the use of exchange materials is continually increasing in industry. When such procedures are being adopted, it is well to remember that their success or failure may depend as much on the nature of the exchange material chosen as on the capacity or stability of the exchanger. The contrast between Permutit and Amberlite in their relative adsorption of K and Ca is an excellent example of the importance of knowing the nature of the exchange material.

Exchange materials are finding increased usage in analytical laboratories as a means of separating and concentrating the rare earth metals. The work of Russell and Pearce (23) is noteworthy in this respect. Through the proper selection of the exchange material and repeated leaching, these investigators have been able to separate the rare earths into groups varying in molecular weight. On the basis of the equilibrium data presented here, it appears that the use of exchange materials as a means of separating ions in solution is a promising procedure. It should, of course, always be remembered that not all exchange materials behave in the same manner, that there is no one exchange material that is best for all types of work, and that exchange capacity is purely a quantitative factor and not an indication of quality.

It is often said that any study made on a soil is limited in its application to the particular soil on which the study was made. With respect to base-exchange equilibria this is not the case. The almost perfect agreement between results obtained for the two soils, kaolin, and illite in this study for both the equilibrium and leaching systems suggests that the data may be applied to a wide variety of soils. In fact, the clay minerals used represent the characteristic exchange minerals of most soils. This does not mean that these soils and soil materials will behave similarly toward all ions, but rather that they do react similarly to the common cations found on the exchange surface of the soil colloid under natural conditions, or as modified by additions of any of the commonly used liming or fertilizer materials.

#### SUMMARY AND CONCLUSIONS

A study was made of some of the factors that were thought to be significant in base-exchange equilibria. The exchange materials studied included natural soils, natural silicate materials, and synthetic exchange materials. Two types of systems were considered; namely, (a) the equilibrium type, in which a definite amount of salt solution is shaken with a definite amount of exchange materials in a closed system and an equilibrium established; and (b) the leaching type, in which a definite amount of exchange material is exhaustively leached with a solution of a definite salt composition and concentration. The following conclusions are based on the experimental data presented:

The  $f$  values obtained by Bray are valid and applicable to surface soils. Slightly lower  $f$  values are obtained for organic-free materials.

The distribution of ions of the same valence on an exchange surface is affected less by the concentration of the solution in an equilibrium system than in a leaching system.

The concentration in solution of ions of different valence does have a marked effect on their final distribution on the exchange material in both types of systems.

The ratio of the ions in a leaching solution is a factor in determining the distribution of those ions on the exchange material.

The distribution of the ions on an exchange surface is controlled to a greater degree by the nature of the colloid or exchange material than it is by any other single factor.

The soluble anion associated with the cations in a leaching solution does not affect the ratio of the bases on the exchange surface but may affect the total amount of bases adsorbed.

Within the limits of these experiments, it may be concluded that soils and natural silicates react as a group in equilibrium as well as in leaching systems, but they differ from the synthetic exchange materials investigated.

Hydrogen was the only cation of those studied that did not behave like the other monovalent cations in the leaching system. Within the range studied, its distribution on an exchange surface does not appear to be a function of its concentration in a leaching solution.

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# FIXATION OF POTASSIUM IN RELATION TO EXCHANGE CAPACITY OF SOILS: III. FACTORS CONTRIBUTING TO THE FIXATION PROCESS<sup>1</sup>

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Peterson and Jennings (23) reported that the exchange capacity of K-treated bentonite was lower than that of bentonite treated with Na or Ca. To explain this they suggested the "possibility that this phenomenon is related to the fixation of K in nonreplaceable forms." Kolodny<sup>3</sup> made a similar observation. Truog and Jones (27) reported that the decrease in exchange capacity was equivalent to the quantity of K fixed. This conclusion, however, was not substantiated by the work of Joffe and Kolodny (13), Levine<sup>4</sup>, and Joffe and Levine (14), all of whom found a general reduction of the exchange capacity when fixation occurred but noted no equivalence between this decrease and the K fixed.

Joffe and Levine (14) saturated two samples of Mantalto clay (diameter 5  $\mu$  and smaller, organic-matter-free) with K. To one of these samples 1.92 m.e. of K was added to the K already present in the exchange complex (1.24 m.e.), whereas to the other no further K was added. Despite the difference in the quantity of extractable K in the two cases, both systems were found to fix equal amounts of K. From this it follows that as long as the complex is saturated with K, the magnitude of fixation will be unaffected no matter how much additional K is applied.

It was also noted that the sample of clay which was K-saturated, but to which no additional K was added, fixed more K than did calcium-, barium-, or hydrogen-saturated clays to which 1.92 m.e. of K was added. This was true despite the fact that the total "free" K (water-soluble plus exchangeable) was less than two thirds that in the case of the variously saturated clays. Again it is obvious that the condition in which the K is present in the system is the determining factor; that is, to be effective for fixation, K must be in the exchange complex.

Drosdoff and Truog (5) demonstrated that the removal of the free Fe and Al oxides from soil colloids has no appreciable effect on the exchange capacity. Such a condition makes it readily apparent that a sample of sesquioxide-free colloid has the same exchange capacity as a larger sample of the untreated colloid. If fixation is a function of the exchange complex, a sample of sesqui-

<sup>1</sup> Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

<sup>2</sup> Temporarily withdrawn; resubmitted September 30, 1946.

<sup>3</sup> Kolodny, L. Mechanism of potassium fixation in soils and the availability of fixed potassium to plants. 1938. (Unpublished doctor's thesis. Copy on file Rutgers University Library, New Brunswick, N. J.)

<sup>4</sup> Levine, A. K. Relation of potassium fixation to the exchange capacity of soils. 1939. (Unpublished master's thesis. Copy on file Rutgers University Library, New Brunswick, N. J.)



oxide-free colloid should fix the same amount of K as a sample of untreated colloid, provided the weights of the respective samples are so chosen that both have the same exchange capacity. Actual experiments with Sassafras colloid bore out this contention.

#### EFFECT OF ALCOHOL ON FIXATION

Wiegner (29) has shown that ions enter the exchange complex more readily in alcoholic solution than in aqueous solution. This he attributed to the dehydration of the ions by the alcohol. Since exchange is favored in alcoholic medium, fixation likewise should be favored when K is the ion exchanged.

Accordingly, bentonite was treated with an alcoholic solution of K-acetate, on the one hand, and an aqueous solution of the same salt, on the other. The quantity of K added in each case was 58.7 mgm. to 5 gm. of bentonite. From the aqueous solution, 17.8 mgm. of K was fixed; from the alcoholic solution, 21.8 mgm. The fact that more K was fixed when alcohol was the solvent than with water is in conformity with the theory presented above.

#### EFFECT OF ANIONS ON FIXATION

Hoagland and Martin (11) and Chaminade (2) reported that the nature of the anion exerts no influence on K fixation. An understanding of the conditions under which these men did their work leads to an explanation of their results. In their work they used anions which exerted very little influence on cation exchange, that is, anions of highly dissociated acids. If, however, the anion is of a weak acid, and if the exchange is carried out against a hydrogen-saturated complex, then there is a well-defined tendency for the anion to combine with the hydrogen ion of the complex. In this case, the cation associated with that anion replaces the hydrogen (24). This phenomenon has been pointed out by Wiegner (30) for the system K-acetate versus hydrogen bentonite:

$$\text{K}^+ + \text{CH}_3\text{COO}^- + \text{H-bentonite} \rightleftharpoons \text{K-bentonite} + \text{CH}_3\text{COOH}$$
where the longer arrow indicates the direction of the equilibrium.

To test this theory, symmetry quantities of KCl and K-acetate were added to 5 gm. of hydrogen bentonite, and fixation was induced. When the acetate was used, 17.7 mg. K was fixed, as compared with 13.7 mgm. fixed with the chloride.

#### EFFECT OF ORGANIC MATTER ON FIXATION

That the exchange reaction is a necessary forerunner of K fixation is evidenced by the effect of additions of organic matter. Gourley and Wanter (8), Sturgis and Moore (26), and Walker and Sturgis (28) have pointed out from field experiments that organic matter exerts a depressive effect on K fixation. This effect is readily explained on the following basis: When organic matter is added to the soil, it competes with the mineral or inorganic fraction of the soil for exchangeable cations, K in this case. Because of its great exchange capacity, the organic matter competes successfully with and diverts considerable quantities of K from the mineral portion. Since organic matter is not capable

of fixing K (12), and since the quantity of K in the inorganic exchange complex has been materially lessened, fixation will be decreased. Thus, fixation may be lessened by a diversion of K from the inorganic exchange complex, and hence the role of the exchange complex in K fixation is further emphasized.

#### EFFECT OF SOLUBLE IRON ON FIXATION

A further means of testing the above theory was suggested by the work of Magistad (16). Working with alkali soils, he was able to reduce the exchange capacity to a very marked degree by treatment with dilute ferric chloride. This phenomenon was noted also by Mattson (17), and by Paver and Marshall (20). If the exchange capacity of a soil can be so reduced, it was felt that fixation, too, should suffer a decrease under the same conditions.

To repeat the work of Magistad, a sample of a solodi from Red River Valley, Minnesota, furnished and described by Rost (25), was used. Four 20-gm. samples of this material were saturated with 0.5 *N* FeCl<sub>3</sub> after the method of Magistad (16). The excess iron was washed out with water. To two of these samples and to two untreated samples 20 m.e. of KCl solution (1 ml. = 5.03

TABLE 13

*Effect of prior ferric chloride treatment on fixation of potassium by solodi soil*  
Results on 100-gm. basis

DESCRIPTION	EXCHANGE CAPACITY BEFORE FIXATION	K FIXED	EXCHANGE CAPACITY AFTER FIXATION
	m.e.	m.e.	m.e.
FeCl <sub>3</sub> treated.....	40.1	0.74	34.0
Not treated.....	44.3	1.37	35.0

mgm. K) was added. The systems were alternately wetted and dried to induce fixation. After fixation, the exchange capacities of the samples were determined. The exchange capacities of FeCl<sub>3</sub>-treated and nontreated systems were also determined when no fixation was induced. The results appear in table 13.

Table 13 bears out the contention that a reduction in exchange capacity results in a lowering of the K fixed. Although the reduction in exchange capacity is not very large, it is nevertheless appreciable and evidently sufficient to cause a marked lowering of the capacity of the soil to fix K. It should be noted that the exchange capacity after fixation does not differ so much in the two cases as does the exchange capacity before fixation. This is to be expected, however, because the greater fixation by nontreated system brings about a more pronounced reduction in the exchange capacity. Why the decrease in exchange capacity exceeds the quantity of K fixed is not apparent from these data, but further light will be shed on this later in this paper. To make sure that the large decrease in exchange capacity was not caused by the wetting and drying, a sample of solodi was wetted and dried, and the exchange capacity determined. The decrease was found to be only 0.5 m.e. per 100 gm.

## BLOCKING FIXATION WITH VARIOUS IONS

That large organic molecules affect the exchange capacity of minerals has been known for some time. Demolon and Barbier (4) pointed out that colloidal humus is strongly taken up by clays. Mattson (18) found the same thing with proteins in place of humus. Myers (19) found that the exchange capacity of a mixture of soil colloids and organic colloids was less than the sum of the two components. Giesekeing (6) observed from x-ray analysis that complex organic cations are exchanged within the variable c-axis of bentonite. More recently Hendricks (10) found that large molecules like the alkaloids brucine and codeine do not neutralize all the hydrogen of a hydrogen-saturated clay. This he attributed to a "cover-up effect"; that is, these alkaloids are so large that in neutralizing some of the hydrogen, the molecules cover up other exchanged hydrogen ions and so make them inaccessible for removal. Thus Hendricks achieved a reduction of the exchange capacity of bentonite by treating the mineral with brucine.

From the above observations, principally that of Hendricks, it was reasoned that if brucine could effectively decrease the exchange capacity of bentonite, it should also lower the ability of the mineral to fix K. Accordingly, a 2-gm. sample of hydrogen bentonite was leached with 500 m.e. of 0.4 per cent brucine solution in alcohol. The sample was then washed with alcohol to remove the excess alkaloid, after which 15 m.e. of alcoholic K-acetate (1 ml. = 3.91 mgm. K) was added, and the system wetted and dried several times. An equal-sized sample of hydrogen bentonite was given like treatment except that it was not saturated with brucine.

The results show that the H-bentonite saturated with brucine fixed 5 mgm. K, whereas the control fixed 7.5 mgm. The reduction in fixation is due to the blocking effect of the brucine. Whatever the mechanism by which brucine decreases the exchange capacity, the effect of such action of fixation is in complete harmony with theory.

## EFFECT OF pH AND Ca ON FIXATION

The literature is replete with reports that lime additions stimulate fixation of K. MacIntire *et al.* (15), investigating the effects of long-term lime and magnesium treatment on the outgo of subsequent additions of K, found that additions of lime to the soil increased fixation. Harris (9) has reported that hydrated lime results in an increase in the quantity of K a soil will fix, and further that the greatest fixation occurs at highest pH values. Some work of Wrenshall and Marcello (31) confirm Harris' observations. Gilligan (7) noted also that K fixation increases with increasing Ca saturation and increasing pH.

The findings of the above investigators are readily explained on the basis of the quantity of K in the exchange complex. Peech and Bradfield (21) have demonstrated that increasing the quantity of Ca in the exchange complex favors the exchange adsorption of K. Working with a number of soils from the Florida citrus belt, Peech (22) found that there is a general increase in the amounts of exchangeable K with increasing pH values or increasing degree of

base saturation. Ayres (1) showed this to be true for a Hilo coast soil from Hawaii. Since, then, more K does enter the exchange complex with increasing pH (increasing the base saturation in the above instances merely led to an increase in the pH of the system), more K is available for fixation, and consequently more K is fixed.

To demonstrate that it is the increase in the pH of the system and not the addition of lime *per se* that causes increased K fixation, the following experiment was conducted in duplicate. To 2.119-gm. samples of hydrogen bentonite

TABLE 14  
*Influence of Ca competition on fixation of potassium by H-bentonite\**

TREATMENT	K FIXED
	mgm.
1 SK†.....	6.4
1 SK + 1 SCa.....	5.1
1 SK + 3 SCa.....	4.6
1 SK + 5 SCa.....	3.9
1 SK + 7 SCa.....	2.5
1 SK + 9 SCa.....	2.1
1 SK + 1 SCa to Na-bentonite.....	9.0

\* Except as noted in last row.

† S denotes symmetry quantity.

TABLE 15  
*Ca-K competition in Utah bentonite*  
Results on 100-gm. basis

CONCENTRATION OF CHLORIDES ADDED	AMOUNT FOUND IN COMPLEX**	
	K	Ca
	m.e.	m.e.
0.2N K, 0.8N Ca.....	19.28	98.57
0.3N K, 0.7N Ca.....	29.67	82.72
0.5N K, 0.5N Ca.....	53.95	56.45
0.7N K, 0.3N Ca.....	69.72	52.41
0.8N K, 0.2N Ca.....	80.78	26.10

\* After Peterson and Jennings (23).

were added respectively: one symmetry quantity of K (25 ml. KCl; 1 ml. = 2.65 mgm. K); one symmetry quantity of K plus one symmetry quantity of Ca (as  $\text{CaCl}_2$ ); and one symmetry K plus 3, 5, 7, and 9 Ca. In addition, one symmetry K plus one symmetry Ca was added to 2.119 gm. of sodium bentonite. The systems were alternately wetted and dried to induce fixation, and the fixations subsequently determined. The data are presented in table 14.

The foregoing experiment also throws some light on the effect of Ca concentration on K fixation when the pH of the system was not appreciably altered. That is, it was reasoned that the large excesses of Ca ions in the system would

be more and more successful in competing with K for exchange positions as the Ca content was raised, and hence a decrease in the amount of K fixed should result. That Ca does successfully compete with K under the conditions outlined has been indicated by Chapman and Kelley (3) and shown by Peterson and Jennings (23). Table 15, taken from Peterson and Jennings, is of interest in this connection.

The data of table 14 are in complete concordance with the requirements of the theory as outlined above. When considered in conjunction with table 15 this is even more apparent, except that the blocking of K by Ca in table 15 is proportional to the quantity of K entering the complex, whereas in table 14 there is no proportionality in fixing K. Hence it is evident that the increase in fixation with lime addition as reported in the literature is due to the increase in pH of the system (by means of which more K is able to enter the complex), rather than to the Ca itself. That adsorption and subsequent fixation when carried out against sodium bentonite are greater than against hydrogen bentonite is to be expected in the light of the great ease with which Na is replaced from the exchange complex.

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## BOOKS

*Dust Storms, 1850-1900.* By JAMES C. MALIN. The Kansas Historical Quarterly, Lawrence, Kansas, 1946. Pp. 71.

This is an interesting study of the records of dust storms in Kansas from 1850 to 1900. The concluding sentence gives a clue to the content of the report. It reads: "There is no reason to assume that dust storms can be prevented altogether, because without question they were frequent and severe prior to white settlement and the plowing of the sod, but the damage incident to agricultural operations should and can be minimized by careful soil management."

*Forest Soils.* By HAROLD J. LUTZ AND ROBERT F. CHANDLER. John Wiley and Sons, Inc., New York, 1946. Pp. 514, figs. 52. Price \$5.25.

This book differs materially from the standard text on soils in that it lays more stress on the natural properties of soils and has little to say on the subject of soil amendments. Among the more interesting new features are the discussions of crystal ionic radii and radius ratios, fauna of forest soils, composition and acidity of forest tree leaves, nature of forest humus layers, effects of forest fires, and ecological relationships in forests. One of the stated objectives of the book is that of recording references to the more important researches on forest soils, as many as 150 completely documented references being appended at the end of a chapter. The book is a highly important contribution to the literature in this field and merits inclusion on all soil reference shelves.

*German-English Science Dictionary.* Second edition, Revised. By LOUIS DEVRIES. McGraw-Hill Book Company, Inc., New York, 1946. Pp. 558. Price \$4.50.

Graduate students who are preparing themselves for examinations in reading scientific German as a part of their requirement for the Ph.D. degree will find this an exceptionally handy and useful volume to have on their study tables. The book has been enlarged about 50 per cent, in considerable part by the inclusion of more terms from the field of agricultural science. Appended to the dictionary are lists of geographic names, abbreviations, chemical elements, thermodynamic symbols, and electric units of measurement.

*Handbook of Chemistry.* Sixth edition. Compiled and edited by NORBERT ADOLPH LANGE. Handbook Publishers, Inc., Sandusky, Ohio, 1946. Pp. 2082. Price \$7.

The sixth edition of this very important handbook differs from the previous one in having a completely revised table of physical constants of inorganic compounds. Some of the data on engineering have been deleted, since they can readily be found in handbooks for specialists in that field. The book begins with first-aid measures and ends with a very valuable index. New subject matter includes an excellent digest on modern concepts of matter, composition



of seawater, periodic arrangement of the elements, ionization constants of acids and bases, electromotive series of metals and alloys, and a number of other features of specialized interest. The book contains much of interest for reading as well as for reference. The editor is entitled to a great deal of credit for having developed such a valuable chemists' aid.

*The Origin, Distribution, and Airphoto Identification of United States Soils.*

By D. S. JENKINS, D. J. BELCHER, L. E. GREGG, AND K. B. WOODS. Technical Report No. 52. U. S. Department of Commerce, Civil Aeronautics Administration, Washington, D. C., 1946. Pp. 201, figs. 86, plates 63.

This report was prepared with special reference to airport and highway engineering but is of considerable interest to soil scientists in general. It is made up of two parts, of which the first is largely descriptive and the second contains large airphotos that are very interesting to study. A bibliography of 772 references is appended, and a large soil map of the United States is contained in a separate envelope.

*Trace Elements in Plants and Animals.* By WALTER STILES. The Macmillan Company, New York, 1946. Pp. 189, figs. 12. Price \$2.50.

This book contains an exceptionally well reasoned presentation of the case for minor nutrient elements in plants. The chapters include: historical introduction, trace-element deficiency diseases of plants, the functions of trace elements in plants, trace elements in animals, and concluding remarks. An extended list of species of plants on which specific effects of one or another of these elements have been noted, together with the name of the respective worker, is an important feature of the book. A list of about 450 references and a well-developed index are appended. Every man who has to do with research in this field of endeavor or who is concerned with the intensive production of plants will find this a very useful reference.

THE EDITORS.

# A CRITICAL EXAMINATION OF A RAPID METHOD FOR DETERMINING ORGANIC CARBON IN SOILS—EFFECT OF VARIATIONS IN DIGESTION CONDITIONS AND OF INORGANIC SOIL CONSTITUENTS

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The method discussed in this paper was tentatively suggested (30) in 1934 to meet the demand for a quick, simple, if approximate, means for determining organic carbon. The procedure was based on the well-known method of Schollenberger (21, 22), the chief difference being the manner in which the digestion was conducted. When concentrated  $\text{H}_2\text{SO}_4$  was added to a mixture of soil and aqueous  $\text{K}_2\text{Cr}_2\text{O}_7$ , the heat of dilution raised the temperature sufficiently to induce a very substantial oxidation within a minute or so. Residual  $\text{K}_2\text{Cr}_2\text{O}_7$  was titrated against ferrous ammonium sulphate as suggested by Schollenberger. Later the method was modified (31) in some of its details.

Trials conducted in 1935 by the International Society of Soil Science and reported by Crowther (5) showed that the method gave more variable results than those employing digestions at higher temperatures and of longer duration. In spite of this it is quite obvious from various publications on soil organic matter which have appeared in the last 10 years, that the method has been used a good deal. Evidently there are many who have rated convenience and speed more highly than accuracy, and who have at the same time demonstrated that the accuracy was sufficient for their purpose. During this period no other methods seem to have displaced the titrimetric ones.

The values obtained by the method were in most instances considerably lower than those obtained by orthodox dry combustion, and a multiplying factor was therefore proposed to bring them more into line with the latter. Some of the causes of the variation of this factor have been briefly mentioned elsewhere (5, 31). It is the purpose of this paper to deal more fully with some of these, and to present new data on other causes of variation, so that the method will have greater utility. Many relevant observations by other workers have also been incorporated.

It is perhaps debatable whether any attempt should ever be made to compare results obtained by an indirect method with those obtained by a direct one. Some prefer that the data be regarded as single values which should stand or fall on their own merits. There are many, however, who would rather think of the results of indirect methods in the units employed by the direct ones.

Some have sought to emphasize the use of the single-value concept in ti-

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trimetric methods on the score that the figure obtained is of value in showing the degree to which soil organic matter has already been oxidized. Such arguments cannot be pushed too far, since the substances easily oxidized by  $\text{CrO}_3$  and other oxidizing agents are not necessarily those readily attacked by microorganisms. It has been found that lignin and cellulose are equally readily attacked in the  $\text{CrO}_3$  digestion, so that the latter in no way simulates the action of organisms which discriminate so sharply between the two.

Whichever viewpoint is held, that is, whether the method is used with or without a multiplying factor, it is important to know the reasons for high or low results. The possible causes of variation have been arranged in three groups as follows:

1. Those due to differences in conditions of digestion and to differences in strength of reagents.
2. Those due to inorganic soil constituents.
3. Those due to variations in the composition of soil organic matter.

Many of the factors involved in group 3 (which are not discussed in this paper) are closely related to those of group 1, because certain types of organic matter are more susceptible than others to variations in oxidizing conditions. However, it is more convenient to separate them in this way.

It is apparent from the literature that a number of workers continue to follow the original procedure, being presumably unaware of the later modifications (5, 31). These, though slight, made for much greater convenience, especially in the handling of large numbers of samples. For this reason, and to serve as a basis for subsequent discussion, the method as it is used now is given below.

#### METHOD

##### *Reagents*

*N Potassium dichromate.* Dissolve 49.04 gm. reagent-grade  $\text{K}_2\text{Cr}_2\text{O}_7$  in water and dilute to 1 liter.

*Sulfuric acid.* Must be at least 96 per cent.

*Phosphoric acid.* Approximately 85 per cent.

*Diphenylamine.* To 0.5 gm. add 20 ml. water and 100 ml. concentrated  $\text{H}_2\text{SO}_4$ .

*N Ferrous sulfate.* Dissolve 278.0 gm. reagent-grade  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in water, add 15 ml. concentrated  $\text{H}_2\text{SO}_4$ , and dilute to 1 liter. Standardize by titration against the *N*  $\text{K}_2\text{Cr}_2\text{O}_7$  solution above. A convenient piece of apparatus designed especially for routine titration, embodying a burette with self-adjusting zero which is filled from a reservoir containing  $\text{FeSO}_4$  kept under hydrogen, is described by Piper (19, p. 225). An alternative method of keeping  $\text{FeSO}_4$  employing a lead amalgam reductor has recently been given by Duke (7). The  $\text{K}_2\text{Cr}_2\text{O}_7$  is delivered from a similar burette mounted over a storage vessel; the  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  are delivered from quick-delivery pipettes with self-adjusting zero fittings.

##### *Procedure*

Grind sufficient soil for convenient sampling to pass a 0.5-mm. screen, avoiding mortars of iron or steel. Transfer a weighed quantity, not exceeding 10 gm. and containing about 10 to 25 mgm. of organic carbon, to a 500-ml. Erlenmeyer flask. Add 10 ml. of  $\text{K}_2\text{Cr}_2\text{O}_7$  followed by 20 ml.<sup>2</sup> of  $\text{H}_2\text{SO}_4$ . Shake the flask once or twice and allow it to stand for 20 to

<sup>2</sup> This amount is incorrectly given as 15 ml. in Tiruin, I. V. The Organic Matter of

30 minutes. Then add 200 to 300 ml. water, 10 ml.  $\text{H}_3\text{PO}_4$ , and 1 ml. diphenylamine solution. Run in  $\text{FeSO}_4$  until the solution is purple or blue. Continue to add  $\text{FeSO}_4$  in portions of about 0.5 ml. until the color flashes to green, which it does with little or no warning. Then add 0.5 ml.  $\text{K}_2\text{Cr}_2\text{O}_7$  and complete the titration by adding  $\text{FeSO}_4$  drop by drop until the last trace of blue disappears. If more than 8 of the 10 ml.  $\text{K}_2\text{Cr}_2\text{O}_7$  originally taken has been reduced, repeat the determination with less soil.

The color is not always purple on adding the indicator at the beginning of the titration, but the color always appears just before the end point. Similarly the purple color often does not appear on the addition of 0.5 ml. excess  $\text{K}_2\text{Cr}_2\text{O}_7$ , but it soon develops with the first drop or two of  $\text{FeSO}_4$ . With more than 10 gm. soil present the color change may become difficult to follow. Large amounts of  $\text{CaSO}_4$  (from calcareous soils) or  $\text{AgCl}$  (if  $\text{Ag}_2\text{SO}_4$  is used to prevent chlorine interference in saline soils) alter the shades of the colors, but the change (now from lavender to pale green) is still just as sharp as before. It has been found convenient to have the flask illuminated brightly from the side by a bench light. The color change is then easily seen in a thin layer of liquid as the flask is shaken.

The percentage of carbon in the soil is given by the following formula:

$$\frac{V_1 - V_2}{W} \times 0.300 \times f$$

where  $V_1$  = volume of  $N$   $\text{FeSO}_4$ , in milliliters, required in blank titration

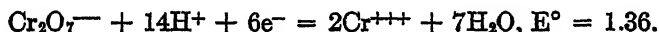
$V_2$  = volume of  $N$   $\text{FeSO}_4$ , in milliliters, required in actual titration

$W$  = weight of soil in grams

$f$  = factor whose value is under discussion. The term "recovery" ( $100/f$ ) is also used.

#### VARIATIONS DUE TO DIFFERENCES IN CONDITIONS OF DIGESTION AND TO DIFFERENCES IN STRENGTH OF REAGENTS

The oxidizing action of acidified dichromate can be represented by the half reaction:



Since the hydrogen-ion activity enters the E. M. F. equation at the high power of 14, increasing acidity will lead to a large increase in oxidizing power. Thus the redox potential of the system depends primarily on the concentration of the  $\text{H}_2\text{SO}_4$ , while the amount of material that can be oxidized depends on the concentration of the  $\text{K}_2\text{Cr}_2\text{O}_7$ . Up to a point at least, then, an increase in recovery of carbon would be expected from an increase in  $\text{H}_2\text{SO}_4$  concentration. This is found to be so in practice. The recovery of carbon, however, also depends on the final temperature obtained during digestion, and obviously there will be some optimum ratio between the volumes of  $\text{H}_2\text{SO}_4$  and aqueous solution yielding the maximum temperature rise. As a result of these two effects, the recovery of carbon first increases with increasing ratio of  $\text{H}_2\text{SO}_4$  to  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, passes through a rather flat maximum, and then decreases. Figure 1 shows the mean recoveries for several soils.

Determinations conducted on some 20 soils using the 15:15 ratio gave consistently lower figures (about 25 per cent) than those on the same soils using the 20:10 ratio. The temperatures obtained were the same in each series, the effect being purely one of higher oxidation potential. The fact that the ratio 20:10 may be decreased to 20:15 without any appreciable fall off in recovery is of importance in determinations on highly calcareous soils low in organic carbon,

for the amount of  $\text{H}_2\text{SO}_4$  neutralized is then appreciable. The 15:15 ratio is quite unsuitable for such soils. In this connection it is interesting to note that Snethlage (26) has shown that the rate of oxidation at  $100^\circ\text{C}$ . of a number of organic compounds has a definite maximum when the  $\text{H}_2\text{SO}_4$  is about 80 per cent by weight. The strength of the acid in the 20:10 mixture is 75 per cent by weight.

The effect of increasing the dichromate concentration while maintaining the ratio of  $\text{H}_2\text{SO}_4$  to aqueous solution at 20:10 is shown in figure 2.

In this trial the size of sample was, of course, appropriate to the strength of dichromate used. Sodium dichromate, being much more soluble than  $\text{K}_2\text{Cr}_2\text{O}_7$ ,

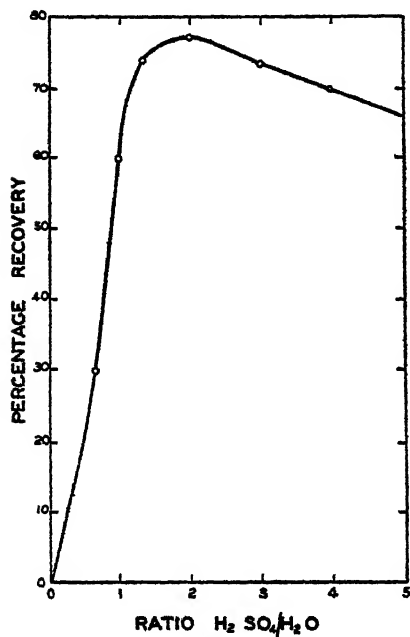


FIG. 1.

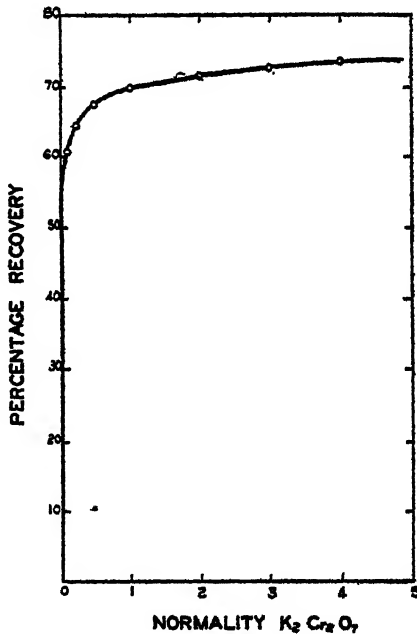


FIG. 2.

FIG. 1. EFFECT OF  $\text{H}_2\text{SO}_4$  CONCENTRATION ON RECOVERY OF CARBONFIG. 2. EFFECT OF  $\text{K}_2\text{Cr}_2\text{O}_7$  CONCENTRATION ON RECOVERY OF CARBON

was used for the last three determinations. The results show that it is not worth while changing over to a stronger dichromate for general use, particularly as the volume required for the titration with  $N \text{FeSO}_4$  then becomes greater and rather unwieldy for a rapid routine method. When dealing with organic soils, however, the use of stronger dichromate has decided advantages, because a correspondingly larger amount of soil can be taken, and sampling errors are thereby reduced. For the determination of organic matter in aqueous extracts it is sufficient to take 5 ml. of sample, add 5 ml. of one of the above solutions of appropriate strength, and then proceed as usual.

The unimportance of the concentration of dichromate is one of the factors

contributing to the success of all titrimetric methods employing it, for the constancy of the oxidation potential throughout the digestion ensures that the last fractions of the organic matter attacked are subjected to the same intensity of oxidation as the first fractions. If this were not so the recovery would depend on the size of sample taken, and a large excess of oxidant would be required to remove this source of error. In the method under discussion it has been found that at least 80 per cent of the  $K_2Cr_2O_7$  can be reduced without affecting the results.

The final temperature reached in the reacting mass clearly depends upon the difference between the heat generated and that lost to the vessel, its contents and surroundings. The following factors are therefore of importance:

*Acid strength.* Experiments on a variety of soils, using acids of strengths varying between 90 and 99 per cent, showed an approximate linear increase of recovery of 1 per cent for every 1 per cent increase in acid strength. With  $H_2SO_4$  containing dissolved  $P_2O_5$ , such as is sometimes used in the Kjeldahl method, further increases in recovery resulted, but these did not seem large enough to warrant departure from the use of a reagent available everywhere. The rate at which the acid is added is not critical. The automatic pipette used in this work delivers  $20 \pm 0.2$  ml. in about 10 seconds.

*Size of reacting vessel.* Pyrex conical flasks of 500 ml. capacity resulted in lower recoveries (about 2 per cent) than when thin-walled 250-ml. flasks were used. The larger size, being more convenient for titration, was preferred, however, and a set of 24 was selected with weights varying between 100 and 130 gm.

*Air temperature.* A number of determinations on several soils with room and reagent temperatures varying from  $15^\circ C.$  to  $30^\circ C.$  showed that all recovery increased by about 1 per cent for every  $5^\circ C.$  rise in air temperature. Variations due to this and to changes in acid strength can be largely eliminated in any one laboratory by conducting one or two determinations on a standard soil with each large batch. This practice has been found useful in correlating results obtained over intervals of time.

Other methods of digestion such as Schollenberger's and Tiurin's (28) define the temperature much more precisely; for example, Schollenberger advises heating his digestion mixture to  $175^\circ C.$  in  $1\frac{1}{2}$  to 2 minutes, whereas Tiurin recommends boiling ( $145^\circ C.$ ) for 5 minutes. Schollenberger (5, 23) has also shown that more consistent results are obtained if 10 ml.  $N K_2Cr_2O_7$  and 10 ml.  $H_2SO_4$  are used for the digestion and the temperature is held at  $140^\circ C.$  for 5 minutes than if 20 ml.  $H_2SO_4$  is used with no external source of heat. In all chromic acid titration methods the object should be to bring about the maximum oxidation of organic matter before any appreciable amount of chromic acid has undergone thermal decomposition. Snethlage (27) has shown that the kinetics of the decomposition are complex and best represented by assuming that two reactions, one monomolecular and the other bimolecular, occur simultaneously. The reaction is positively catalyzed by  $Cr_2(SO_4)_3$ , which is the main product of reduction, and probably by other substances. Ignited soil is one such substance and probably unignited soil also, but because of the difficulty of preparing an unignited soil devoid of organic matter it is difficult to establish the magnitude of the effect. The decomposition proceeds more rapidly as the  $H_2SO_4$  concentration increases, and for this reason mixtures in the ratio of 2

$\text{H}_2\text{SO}_4$  to 1 aqueous solution cannot be boiled for long in the presence of catalysts without undergoing considerable decomposition. This fact was thoroughly appreciated by Tiurin (who uses a 1:1 ratio) in framing his method, and by Schollenberger in suggesting the 1:1 modification just referred to.

Several workers have reported the results obtained by supplementing the heat of dilution of the 2:1 mixture with an external source of heat. Smolik (25) boiled the mixture for 1 minute and claimed good agreement with the Densstedt method on 30 different soils. On the other hand, Novák and Pelisek (18), using the same procedure, obtained excessively high results (as would be expected if there was much decomposition of  $\text{CrO}_3$ ) and so reverted to the original procedure for the remainder of their study of the method. Similarly some of the results of Kelley and Thomas (11), who heated the mixture in a water bath (presumably at  $100^\circ\text{C}$ .) for 15 minutes, were unusually high. Whether there is any appreciable thermal decomposition of  $\text{CrO}_3$  in the course of a normal determination when the temperature is raised suddenly by the heat of dilution alone to about  $110$ – $120^\circ\text{C}$ . and then allowed to cool cannot be stated. There is certainly none in the absence of soil and none in the presence of a large variety of ignited soils.

Silver salts either in the form of  $\text{Ag}_2\text{Cr}_2\text{O}_7$  or  $\text{Ag}_2\text{SO}_4$  have been used (5) as catalysts in  $\text{CrO}_3$  digestions, the object being to catalyze the oxidation of CO to  $\text{CO}_2$ . Whether or not this is the mode of action, higher results are usually obtained when a silver salt is present, the effect being greatest with Tiurin's method of digestion, less with Schollenberger's, and least with the Walkley-Black method (5, 29). Some recent experiments on a variety of soils have shown that the increase in the last method is rarely more than 3 per cent. Since in all three methods the results obtained with added  $\text{Ag}_2\text{SO}_4$ , though higher, are more consistent, there seems little justification for the use of this salt.

In the method as originally described the soil was first ground to 100 mesh. Subsequent experiments showed that grinding to  $\frac{1}{2}$  mm. was sufficient, and this standard of size has been adopted throughout the present work. More recently results have indicated that the extent of oxidation is much the same even in soils of 1 or 2 mm. size. It appears probable then that considerations of sampling alone should decide whether grinding is necessary. If it can be dispensed with, a considerable saving of time will result in routine determinations.

Another change which makes for greater convenience is to omit the 1-minute shaking. The  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is added to each flask (24 is a suitable number for a batch), then acid to the first flask, and this after one or two shakes, is set aside while acid is added to the next. When the acid has been added to the last flask, the first is ready for dilution and titration. No appreciable differences have been observed with times of standing varying between 5 and 40 minutes.

Other indicators have been suggested for the titration including *o*-phenanthroline (1, 4) barium diphenylamine sulfonate (1), and phenylanthranilic acid (12). After these were tried, the conclusion was reached that preference for any one is largely a matter of personal taste. In a survey of some 300 Australian soils no sample was found in which the end point could not be recognized

to within 1 or 2 drops of diphenylamine. Smith and Weldon (24) prefer to add excess ferrous ammonium sulfate and back titrate with  $\text{KMnO}_4$ ; Novák and Pelisek (18) do likewise but back titrate with  $\text{K}_2\text{Cr}_2\text{O}_7$ .

It will be seen that by the combined effect of using 100 per cent  $\text{H}_2\text{SO}_4$ , 3 *N*  $\text{Na}_2\text{Cr}_2\text{O}_7$ , and  $\text{Ag}_2\text{SO}_4$ , it might be possible to raise the recovery of carbon in many soils by some 5 per cent or more. There can be no doubt, however, that the inconvenience would outweigh the advantages. Substantial increase in recovery can probably be achieved only by increasing the time and temperature of digestion. Suitable procedures already exist embodying these refinements (23, 29). This fact having been realized early, the aim of subsequent investigations was to examine the magnitude of the causes of variation rather than to attempt to eliminate them. Variations due to several inorganic oxidizing and reducing agents, however, can be eliminated by appropriate modifications of the method.

#### EFFECT OF SOME INORGANIC CONSTITUENTS

##### *Calcium carbonate*

The fact that  $\text{CaCO}_3$  is without influence in titrimetric methods has always been one of the strongest arguments in favor of such methods, particularly for the examination of highly calcareous soils deficient in organic matter, where the complete removal of the carbonate prior to dry combustion is tedious and difficult in many instances. Even when a 10-gm. sample of soil containing 50 per cent  $\text{CaCO}_3$  is taken for analysis, only about 5 gm., or one seventh, of the total amount of  $\text{H}_2\text{SO}_4$  is utilized in neutralization. This diminution in strength, as was shown earlier, is not sufficient to affect appreciably the intensity of attack on organic matter. Any slight effect is probably more than compensated by the slightly increased temperature due to the neutralization reaction. The unimportance of  $\text{CaCO}_3$  has been proved by adding 5 gm.  $\text{CaCO}_3$  to a number of soils prior to determining the carbon content. The increases in recovery over those for the untreated soils did not exceed 2 per cent. Successful trials of the method on large numbers of calcareous soils have also been conducted.

##### *Chlorides*

The disturbing effect of soluble chlorides has been examined in detail and reported elsewhere (31). It was shown that the reaction between the dichromate and the chloride proceeded in such a way that the former was reduced quantitatively, thus permitting the accurate application of a correction factor. The correction consists in subtracting one twelfth of the chlorine content from the apparent carbon content. (1 atom C  $\equiv$  4 atoms Cl, and  $12.0/4 \times 35.5 \approx 1/12$ ). It was found to be valid up to a Cl:C ratio of 5:1.

Alternatively the oxidation of the chloride can be prevented by using  $\text{H}_2\text{SO}_4$  containing 25 gm.  $\text{Ag}_2\text{SO}_4$  per liter for the digestion. Mercuric oxide and mercuric sulfate were found equally effective. The latter has also been found satisfactory for immobilizing chlorine in nitrogen digestions (17). Ratios of



Cl:C up to 5:1 have been encountered in a series of marine swamp soils near Adelaide, South Australia. Their analysis showed that when the correction factors were applied, the correlation with dry combustion figures was as high as for other groups of nonsaline soils.

### *Higher oxides of manganese*

The forms in which the higher oxides of manganese exist in the soil are not known. Recent x-ray diffraction studies (8, 15)<sup>3</sup> have shown that there are four or five different modifications of the oxide approximating to the formula  $\text{MnO}_2$ , apart from several modifications of that approximating to the formula  $\text{Mn}_2\text{O}_3$ , as well as  $\text{Mn}_3\text{O}_4$ . Many of the oxides show a deficiency of oxygen; for example, the higher oxides show a departure from the stoichiometric formula  $\text{MnO}_n$ , where  $n = 2$ . Thus though it appears that pyrolusites, whether natural or artificial, have values of  $n$  very close to 2, yet for certain other oxides prepared in the wet way,  $n$  may be as low as 1.7 or 1.8 and still retain the same structure as an oxide for which  $n = 1.97$ . Such low values may be due to absorbed manganoous ion, or to an actual defect of oxygen in the lattice, or to both. In any event the oxygen readily available ("active oxygen") is probably  $n-1$  atoms of oxygen per atom of manganese.

Besides differences in crystal form and content of active oxygen, large differences in reactivity are found. D'Agostino (6) showed that there were big differences between the rates at which different oxides reacted with acidified oxalic acid, his method being to measure gasometrically the rate of production

of  $\text{CO}_2$ ,  $\left(\frac{dv}{dt}\right)$ . Still bigger differences in  $\left(\frac{dv}{dt}\right)$  have been found by Wadsley and

Walkley<sup>4</sup> in an examination of a number of ores and chemically prepared manganese oxides, the highest value for an ore being about 30 times that for the most slowly reacting ore, and the highest value for a chemically prepared oxide being about five times greater again. There is no obvious correlation between reactivity and structural type. It seems probable at present that surface area is the chief factor responsible, though lattice imperfections and defects also doubtless play a part.

There seems no reason why all the structural forms found in ore bodies should not occur in soils. But what is probably more important, the range of reactivities (D'Agostino values) encountered in natural and chemically prepared samples could almost certainly occur in soils. Such a range of reactivities would be quite sufficient to account for the differences in the percentage of total manganese reduced and leached from various soils by buffered quinol solutions (14).

When  $\text{MnO}_2$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  are heated with an oxidizable substance in the presence of an acid, the two oxidizing agents compete with each another, and the proportion of the total oxidation effected by the  $\text{MnO}_2$  depends on its re-

<sup>3</sup> Cole, W. F., Wadsley, A. D. and Walkley, A. Unpublished work, 1946.

<sup>4</sup> Wadsley, A. D. and Walkley, A. Unpublished work, 1946.

activity. Thus even if the active oxygen content of the soil were known accurately, it would not be possible to correct for it. This difference in behavior of different oxides is well shown in the results (table 1) of several experiments where samples of oxides in amounts equivalent to 0.200 gm.  $\text{MnO}_2$ , were added to 0.040 gm. sucrose and digested as usual. After dilution with water the digests were filtered through sintered glass to remove unattacked oxide, and the filtrate was titrated with  $\text{FeSO}_4$ . Determinations were also conducted in the absence of  $\text{MnO}_2$  to serve as standard. The amounts of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{MnO}_2$  were sufficient for each to oxidize all the sucrose completely even if the other were absent.

Clearly the rate of attack by the first three ores is so slow that the sucrose is oxidized almost entirely by the  $\text{K}_2\text{Cr}_2\text{O}_7$  and only the artificial oxide plays any important part. The correspondence between the figures in the last two columns

TABLE 1  
*Fraction of sucrose oxidized by samples of  $\text{MnO}_2$  of different origins*  
0.200 gm.  $\text{MnO}_2$  added to 0.40 gm. sucrose

ORIGIN OF OXIDE	MINERAL COMPOSITION*	D'AGOSTINO VALUE $\left(\frac{ds}{dt}\right)^\dagger$	PERCENTAGE OF SUCROSE OXIDIZED BY $\text{MnO}_2$
Gold Coast ore.....	$\gamma$ $\text{MnO}_2$ mostly; some pyrolusite	0.14	<1
Western Australian ore.....	Cryptomelane	0.19	<1
South Australian ore.....	Pyrolusite	0.48	<1
New Zealand ore.....	$\gamma$ $\text{MnO}_2$ and cryptomelane	2.0	6
Chemically prepared oxide.....	Unknown oxide with layer lattice structure	8.0	49
Chemically prepared oxide $^\ddagger$			21

\* See text footnote 3.

† See text footnote 4.

‡ Same sample as preceding, but only 0.100 gm.  $\text{MnO}_2$  added.

suggests that the D'Agostino value gives a good indication of the amount of disturbance in the method likely to be caused by any one type of  $\text{MnO}_2$ . The most reactive type represented here may perhaps correspond to the freshly precipitated soil manganese which is in circulation, which readily takes part in oxidation reduction reactions, and which is therefore of significance in the nutrition of the plant; whereas the least reactive types may correspond more to the inert reserve material. In normal soils the amounts of such readily reducible oxide will certainly be small, and even in highly manganiferous soils it does not seem likely that there would be more than a small fraction of the whole present in this state. It is considered that the average reactivities of the oxides in any one manganiferous soil is more likely to be nearer those of the first four samples, and therefore with the ratio  $\text{MnO}_2$  to carbon existing there (8.5:1) the error in the carbon determinations would be only 0 to 6 per cent. The highest ratio reported in the Waite Institute collection of Australian soils was 0.8, the soil in question (a basaltic red loam from Queensland) having the

most serious quinhydrone error of a number examined by Best (3). The recovery of carbon was 72 per cent, which is not abnormal, and subsequent examination of a series of 30 similar soils confirmed that the magnitude of the error was very small in all instances. The method has been reported (32) successful on a variety of Hawaiian soils, though no mention was made of whether these were the highly manganiferous soils.

If large quantities of very reactive oxides should be encountered, their effect can readily be annulled by a preliminary treatment with  $\text{FeSO}_4$ . Such active oxides react rapidly with cold acidified  $N$   $\text{FeSO}_4$ , and their amount can thus be determined by a preliminary titration. Two milliliters  $\text{H}_3\text{PO}_4$ , 5 ml. of water, and 1 ml. indicator are added to the soil, followed by sufficient  $N$   $\text{FeSO}_4$  to give an excess as judged by the color of the indicator (5 ml. will usually suffice). The mixture is allowed to stand with an occasional shake for 10 minutes and the excess  $\text{FeSO}_4$  is titrated with  $\text{K}_2\text{Cr}_2\text{O}_7$ . The amount of  $\text{FeSO}_4$  oxidized by the  $\text{MnO}_2$ , as determined by this titration, is then added to a fresh sample of soil

TABLE 2

*Effect of  $\text{FeSO}_4$  in removing disturbance due to reactive  $\text{MnO}_2$  in carbon determinations*

	$\frac{\text{MnO}_2}{\text{C}}$	CARBON CONTENT FOUND
		<i>per cent</i>
Soil alone.....	..	1.06
Soil plus chemically prepared oxide.....	10	0.45
Soil plus chemically prepared oxide, with $\text{FeSO}_4$ pretreatment.....	10	1.02
Soil plus Gold Coast ore.....	10	1.02
Soil plus Gold Coast ore, with $\text{FeSO}_4$ pretreatment.....	10	1.09

together with 2 ml.  $\text{H}_3\text{PO}_4$ . After standing about 5 minutes, most of the  $\text{MnO}_2$  will have dissolved, and what remains may be neglected. Ten milliliters  $N$   $\text{K}_2\text{Cr}_2\text{O}_7$  is then added and the digestion conducted as usual.

The effectiveness of this simple method of pretreatment is clearly shown in table 2. Soil samples to which 10 per cent of reactive and 10 per cent of unreactive oxides had been added were digested with and without  $\text{FeSO}_4$  pretreatment. The results also show that the pretreatment, though effective, is unnecessary for such unreactive material as Gold Coast ore.

#### *Reduced iron*

There can be no doubt that soluble ferrous compounds, if present, will lead to high results. The only question at issue is the prevalence of such compounds (9). Lee (13), in a study on the utility of rapid titration methods in paddy soils, quoted results which show that in gleied subsoils the results may be very high. He used Tiurin's  $\text{CrO}_3$  method and Istscherekov's (10)  $\text{KMnO}_4$  method. In these horizons he found that the ferrous iron, as shown by Morgan's rapid approximate method (16), was also high. He rightly pointed out that lack of an

adequate method makes it impossible to distinguish reduction due to organic matter from that due to ferrous salts or to any other reducing agents. The same reasons prevent the application of any accurate correction.

A considerable number of swamp soils from different parts of Australia have been examined by this method and found to give normal recovery figures. In all instances the samples were air-dry. Had they been examined straight from the field the results might well have been different. Some of these soils were from marine swamps (already referred to) which were covered by the tides daily; others were from fresh-water swamps. In some instances the fresh samples smelled strongly of  $\text{H}_2\text{S}$ . In spite of this, air-drying for a day or two apparently allowed oxidation to occur to such an extent that the recovery figures all fell within the range of normal agricultural soils. The results of determinations by the method on a wide variety of soils and subsoils have made it quite obvious that the amounts of soluble ferrous compounds in air-dried samples are usually trifling compared with the content of organic carbon.

#### *Elementary carbon*

It is convenient to treat elementary carbon among the various inorganic components, for like them, and unlike soil organic matter, it is not universally present. Moreover, it has long been recognized as a source of disturbance in methods for determining the organic matter. As with the manganese oxides, the magnitude of the disturbance due to carbon depends on its reactivity. Riley (20) has examined the rate of oxidation of different forms of elementary carbon by means of  $\text{CrO}_3$ - $\text{H}_3\text{PO}_4$  and  $\text{CrO}_3$ - $\text{H}_2\text{SO}_4$  mixtures and has shown that the rate of attack depends not only on the surface area, but also on the nature of the carbon, the most highly graphitized forms reacting most quickly. He has produced evidence which suggests that the accessibility to the chromic acid of the hexagon layer surfaces of the graphite crystallites is reduced by the presence of hydrogen or residual hydrocarbons which are bonded to these surfaces. The higher the carbonization temperatures, the less of these bonded materials will be present.

The results of some determinations by the soil digestion method on a few samples of elementary carbon are shown in table 3. The samples are merely finer than 70 mesh and so are not necessarily comparable in surface area.

The last sample, although the most highly graphitized, had a lower recovery than most of the others. This may be accounted for by the fact that it was the coarsest of all, flake graphite being always difficult to grind. Oxidation of this sample stopped at the graphite oxide stage, as could be readily detected by filtering the residue and then washing and warming it, when the swelling reaction typical of such lamellar compounds occurred.

It is clear that the recoveries are in all instances much less than those found for soil organic matter. When a sample of the wood charcoal listed in table 3 was added to soil of known carbon content and both were digested together, the recovery of charcoal carbon was even less, being only 6 per cent. As the composite soil contained 1.4 per cent organic carbon and 3.9 per cent charcoal

carbon, the dry combustion method would have indicated 5.3 per cent total carbon. On the other hand, the carbon content as revealed by the rapid titrimetric method was 1.6 per cent (using a multiplying factor of 1.3). The method has thus discriminated well between the two varieties of carbon. Soils rich in elementary carbon may sometimes be detected by their wide C:N ratio (in the foregoing instance 50:1) and sometimes by inspection of the coarse fraction. From Riley's work it does not seem likely that forms of carbon more reactive than natural graphite need be considered. This is sometimes seen as shining flakes in soils derived from graphitic schists.

If the oxidations are prolonged, the recoveries increase. The same sample of charcoal when digested by Tiurin's method gave an 84 per cent recovery of carbon. Schollenberger's digestion was not tried, but it is possible that the result would have been lower, for as Balfour *et al.* (2) showed, the optimum digestion rate occurs with acids between 70 and 90 per cent, whereas Schollenberger uses concentrated  $\text{H}_2\text{SO}_4$ . Allison (1) has quoted an example to show

TABLE 3  
*Recoveries of several varieties of elementary carbon by soil digestion method*

	CARBON CONTENT	CARBON RECOVERY
	<i>per cent</i>	<i>per cent</i>
Bituminous coal.....	78	11
Gas coke.....	93	2
Wood charcoal.....	79	11
Natural microcrystalline graphite (Queensland).....	88	10
Natural flake graphite (South Australia).....	94	4

that his modification of Schollenberger's method discriminates between organic carbon and that in the form of cinders and coal, though the actual amounts of such materials present are not stated.

#### CONCLUSIONS

It has been shown that differences in conditions of digestion and in strength of reagents are chiefly of importance insofar as they determine the final temperature attained. The concentration of  $\text{H}_2\text{SO}_4$  is of importance, but the concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$  is not. Boiling the 2:1  $\text{H}_2\text{SO}_4$ : $\text{K}_2\text{Cr}_2\text{O}_7$  mixture with the object of attaining a constant and reproducible temperature is not permissible, but the reproducibility required to tie up results obtained over a period of time can be achieved by the inclusion of a standard soil in each batch of analyses.

The effect of  $\text{CaCO}_3$  can be neglected, and that due to soluble chlorides can be readily allowed for. The effects due to reduced iron, higher oxides of manganese, and elemental carbon cannot be allowed for, but evidence has been presented in each instance which shows either the unimportance of the error or its probable limiting magnitude. A modification of the method can be used to eliminate the effect of the manganese oxides in the few instances where this may be neces-

sary. The main causes of variation in the recovery factor are thus not any of the foregoing, but are undoubtedly to be found in the variable nature of the soil organic matter itself.

#### SUMMARY

The causes of variation in the recovery factor of the Walkley-Black method have been separated into three groups, two of which are discussed here.

In the first, the magnitude of the effects due to strength of  $H_2SO_4$  and of  $K_2Cr_2O_7$ , to time and temperature of digestion, and to addition of catalysts, has been investigated.

In the second, the effects of  $CaCO_3$ , soluble chlorides, higher oxides of Mn, reduced Fe, and elementary C have been critically examined.

Several of the causes can be eliminated or allowed for. Where this is not possible, the errors can be shown to be unimportant in most instances.

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# MEASUREMENT OF THE OXIDATION-REDUCTION POTENTIALS OF NORMAL AND INUNDATED SOILS

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Many investigators have measured the oxidation-reduction potential of soils by very different methods. For the most part, the redox potential has been measured in soil suspensions. Yet it is commonly observed that the use of suspensions and of extracts of soil yields unreproducible data because of a very inconvenient negative drift of the potentials measured at the electrodes. Moreover, the results, being mainly the expression of certain chemical characteristics of the soil, rarely reflect the aerobic or anaerobic condition. As a result, the carrying out of measurements in undisturbed soils has come to be preferred. Starkey and Wight (4) recently reviewed the methods used by previous investigators and also described a method by which the redox potential could be determined in the field at great depths.

In attempts to measure the potential of freshly reclaimed soils of the Zuiderzee and of soils flooded with salt water during the war in the southern part of Holland, many difficulties were encountered. As the most recent literature on this subject was not available, it was necessary to develop a new method for the measurement of the redox potential of soils. Subsequently, when this method was compared with the most recent method used by Starkey and Wight (4), certain essential differences appeared. It seems worth while, therefore, to publish the details of our own method, together with its theoretical basis. When this method was applied to soils flooded with water during the war, some very interesting data, which gave some insight into the factors influencing the redox potential of soils, were obtained.

## THEORETICAL CONSIDERATIONS

The redox potential of a soil is determined by the antagonistic influence of reducing substances and oxygen. This is well illustrated by the following experiments:

During an investigation of a strongly reduced black clay from the polder "Urkerland," a 1:10 suspension of the soil was made and distributed in a series of glass tubes of large diameter. In these tubes the pH of the suspensions was altered by the addition of either  $H_2SO_4$  or NaOH. After the suspensions had settled, the Eh and the pH were measured in the sediment and in the clear supernatant liquid. The relation between Eh and pH is shown in figure 1. Almost identical curves were obtained by determining the relation between Eh and pH in a 1:10 suspension of kaolin in which FeS had been precipitated (100 gm.

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kaolin, 540 mgm.  $\text{FeSO}_4$ , 400 mgm.  $\text{Na}_2\text{S}$  in 200 cc water). Here, too, the suspension was made acid with  $\text{H}_2\text{SO}_4$  and alkaline with  $\text{NaOH}$ . The rise in the curves of the supernatant liquid between pH 6 and 7 must have been produced by  $\text{FeS}$ , which forms the more soluble  $\text{H}_2\text{S}$  in acid medium. In consequence, the capacity of  $\text{S}^{2-}$  in the liquid is greater in acid medium than in alkaline medium, so that another redox potential is observed. In the sediment, where the concentration of oxygen can be disregarded in view of the much greater concentration of the sulfide, the potential is determined by the sulfide alone and, in consequence, is independent of its concentration. In these experiments the potentiometric results could be confirmed by colorimetric observations with 2-6-dichlorophenol-indophenol, one of the few dyes not fully absorbed by soil.

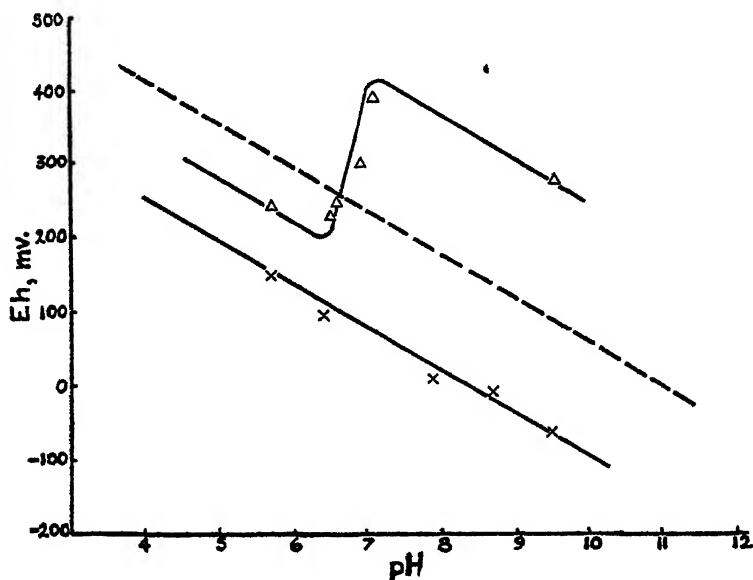


FIG. 1. Eh and pH in a 1:1 Suspension of a Reduced Soil from the Polder "Urkerland" Measured with Bright Platinum Electrodes

The pH was changed with  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ .

× — × Measurements in the sediment.

Δ — Δ Measurements in the clear supernatant liquid.

— — — Eh-pH relation of 2-6-dichlorophenol-indophenol.

From these experiments the conclusion may be drawn that in soils containing  $\text{FeS}$  the potential is mainly determined by the mutual relation between the capacity of oxygen and the capacity of sulfide ions. In other soils the presence of reducing organic substances and bacteria may be equally important. Of course, the equilibrium between these reducing substances and oxygen is very unstable. Every disturbance of the equilibrium, either by changing the concentration of oxygen or by changing the activity of the reducing substances, must, therefore, be avoided. In consequence, the measurement of the redox potential should be made either in the field or in a sample of the soil brought to the laboratory in an undisturbed condition. Since the introduction of the

electrodes in itself produces a disturbance of the soil equilibrium, one should wait until equilibrium has become re-established before measuring the redox potential.

When no reducing substances are present and the soil is well aerated, the potential will be mainly determined by oxygen. As there is no reason to assume the presence of well-poised redox systems in all kinds of soils, the chief problem in determining redox potentials of many soils may be that there are difficulties in obtaining accurate measurements, for there may be potential changes during sampling. In such systems the following difficulties (3, pp. 20-24) are encountered:

1. The reaction  $C_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$  is very slow and is not catalyzed by bright platinum to a degree that would make possible the manifestation of a stable potential at the electrodes.

TABLE 1

*Redox potentials of poorly poised and of well-poised solutions and of soil suspensions as measured with electrodes of bright platinum and of platinized platinum*

Eh in millivolts

	DISTILLED WATER	TAP WATER	BORATE BUFFER	PHthalate BUFFER	SOLUTION OF $FeCl_3$ AND $FeCl_2$	ASCORBIC ACID, 0.01 PER CENT	ASCORBIC ACID, 0.1 PER CENT	ASCORBIC acid, 1 per cent	SUSPENSION AERATED SOIL	SUSPENSION REDUCED SOIL
pH, glass electrode...	5.24	6.02	9.24	3.97	....	4.65	3.43	2.70	7.58	7.45
Eh, bright Pt.....	409	436	402	628	704	346	344	329	510	23
Eh, bright Pt.....	605	437	400	657	697	350	342	329	425	-36
Eh, bright Pt.....	481	473	423	696	704	321	337	333	661	46
Eh, black Pt. ....	736	665	456	799	710	586	337	325	493	27
Eh, black Pt. ....	730	671	446	793	710	600	337	326	494	30
Eh, black Pt. ....	732	673	450	800	712	589	340	329	499	28

2. Electrodes of platinum do not behave as indifferent electrodes when measuring high potentials of oxygen, as it has been shown by many authors that the surfaces of the electrodes are covered by a very thin layer of oxides. This layer is of no importance when measuring the redox potential of solutions sufficiently reducing to dissociate the ions of the platinum. Nor does it cause trouble when a redox system with a sufficiently poisoning capacity is present in the solution. On the other hand, in aerated suspensions in which poisoning systems are lacking, the potentials measured at electrodes of bright platinum are much too low and are poorly reproducible. It might be expected that the potential in poorly poised solutions would be more easily measured with electrodes of platinized (black) platinum, since the reaction velocity of oxygen is catalyzed by the presence of black platinum.

Table 1 presents a series of measurements performed with electrodes of black platinum and electrodes of bright platinum in solutions with a different poisoning capacity. All measurements were performed in open beakers. The electrodes

were platinized in the manner described below. The redox measurements were made with a Coleman potentiometer and the pH measurements with a glass electrode and the same apparatus.

It is evident that the results with electrodes of black platinum are more nearly reproducible than are those with electrodes of bright platinum. Furthermore, the potentials measured with electrodes of bright platinum are, for the most part, far lower than those measured with black platinum, though even the latter potentials are lower than the theoretical values. The relation between Eh and pH as measured with black electrodes agrees fairly well with the theoretical 0.06 relation. Furthermore, it appears from table 1 that the reproducibility of the measurements with electrodes of bright platinum is increased when well-poised redox systems are present in the solution. In such instances the measurements with bright platinum reach the same level as the measurements with black platinum. The

TABLE 2

*Redox potentials of tap water as measured with electrodes of bright and of platinized platinum which were treated with  $KMnO_4$ , tap water, or ascorbic acid previous to the measurement*

Eh in millivolts

PREVIOUS TREATMENT WITH.....	$KMnO_4$ , 0.05 PER CENT		TAP WATER		ASCORBIC ACID, 0.1 PER CENT	
TYPE OF ELECTRODE .....	Bright	Black	Bright	Black	Bright	Black
Interval between introduction of electrode and measurement						
15 minutes.....	833	950	514	684	448	602
45 minutes.....	792	872	504	666	442	656
2 hours 15 minutes.....	732	784	506	651	436	657
4 hours 15 minutes.....	698	712	473	636	411	643
20 hours.....	666	619	491	610	405	617

two observations in soil suspensions show definitely that here, too, the use of black electrodes is preferable, particularly when well-aerated soils are being tested. This was to be expected, as the solubility of iron ions (one of the most important poisoning systems in soils) increases when the pH and the Eh decrease. The superiority of black electrodes, therefore, will be most pronounced in alkaline and well-aerated soils.

It is a well-known fact that the potential measured with electrodes of bright platinum in poorly poised solutions is greatly influenced by the potential previously measured. With platinized electrodes this difficulty is eliminated, since the surface of the electrodes can be constantly renewed by replatinization. Moreover, the effect of previous measurements is less pronounced with black electrodes. Table 2 presents measurements of the redox potential of tap water with both types of electrode subjected to a previous treatment with oxidizing or reducing substances.

It is evident that the platinized electrodes are much less adversely affected

than are the bright electrodes by previous use in solutions containing oxidizing or reducing substances, for after only 20 hours the three black electrodes showed the same potentials, while the three bright electrodes still differed by 261 millivolts. (The gradual decrease of the potential, even in the control, is caused by a real decrease of the potential of the poorly poised water, not by an alteration of the electrodes.)

The data in tables 1 and 2 show clearly the superiority of black electrodes when measuring potentials in poorly poised systems. Though black electrodes give reproducible results, the results obtained with bright electrodes are often entirely a function of the oxides on the surface of the platinum. The potentials of many soils are much better poised than those of tap water. It is useless, therefore, to test the electrodes in solutions of quinhydrone prior to making soil measurements, as recommended by Bradfield *et al.* (1). The electrodes must be tested in solutions less well poised than the soil, not in solutions better poised. We often observed that electrodes of bright platinum cleaned by heating to redness in an alcohol flame and showing the correct potential within an accuracy of 1 millivolt in solutions of quinhydrone gave potentials differing from one another by more than 100 millivolts in poorly poised solutions and in certain soil suspensions. Only those electrodes which give reproducible results in poorly poised solutions (for example tap water) will give reliable results in all kinds of soils. Thus, in practice, only platinized electrodes are satisfactory.

#### METHOD OF MEASURING OXIDATION-REDUCTION POTENTIALS OF SOILS

The following method, based on the conclusions reached in the preceding section, was used for measuring the redox potentials of soils:

When the oxidation-reduction potential cannot be measured in the field, the soil should be brought to the laboratory in an undisturbed condition. This can be done with the apparatus shown in figure 2. The hollow cylinder *A*, which is sharpened at the lower end, is driven into the soil. Then the soil surrounding the cylinder is excavated and the cylinder containing the soil is removed and carefully closed at the bottom with the piece of rubber *B*, which is held firmly against the cylinder by the strong springs *C*. Though in this way the soil can be removed without much disturbance, the procedure is still far from ideal; consequently, the measurements of redox potentials should be made in the field, if possible.

Platinum wires 0.5 mm. thick and 2 cm. long, which have been melted into glass tubes 0.5 cm. in diameter, are used as electrodes. The length of the wire protruding from the glass is  $\pm 1.5$  cm. Contact with the copper wire leading to the potentiometer is made by soldering as recommended by Buehrer *et al.* (2). The electrodes are platinized in the usual way by putting them, as the cathode, into a solution containing 2 to 3 per cent  $\text{H}_2\text{PtCl}_6$  and a trace of lead acetate. As the anode, a piece of platinum is hung into the solution. The poles are connected with a 4-volt battery for 5 minutes, after which the electrodes are rinsed with water and put into a solution of 3 per cent  $\text{H}_2\text{SO}_4$  and connected to the battery as before, the current being allowed to flow 2 minutes.

After platinization, the electrodes are kept in distilled water for 24 hours. Before use they are hung close together in a beaker containing a buffer solution, and the *Eh* is measured at each electrode. It was found that usually the potentials did not differ from one another by more than 10 millivolts. Electrodes showing potentials differing more than 20 millivolts from the mean value were rejected.

After use in the soil, the electrodes must be replatinized. This is done by placing

them, as the anode, in a solution of 2 to 3 per cent  $\text{H}_2\text{PtCl}_6$  for 5 minutes, after which they are platinized as previously described.

A glass tube of the same diameter as the tube of the electrode is first put into the soil, and the electrode is then inserted in the hole thus produced. Then the electrode is pushed 1 cm. farther into the soil, in order to establish a good contact. The soil surrounding the electrode is lightly pressed against it to prevent diffusion of oxygen between the glass of the electrode and the soil particles. The redox potential of the soil is usually measured 2 days after the introduction of the electrodes. The potential is measured against a saturated calomel electrode, using a portable vacuum-tube potentiometer<sub>2</sub> (Coleman).

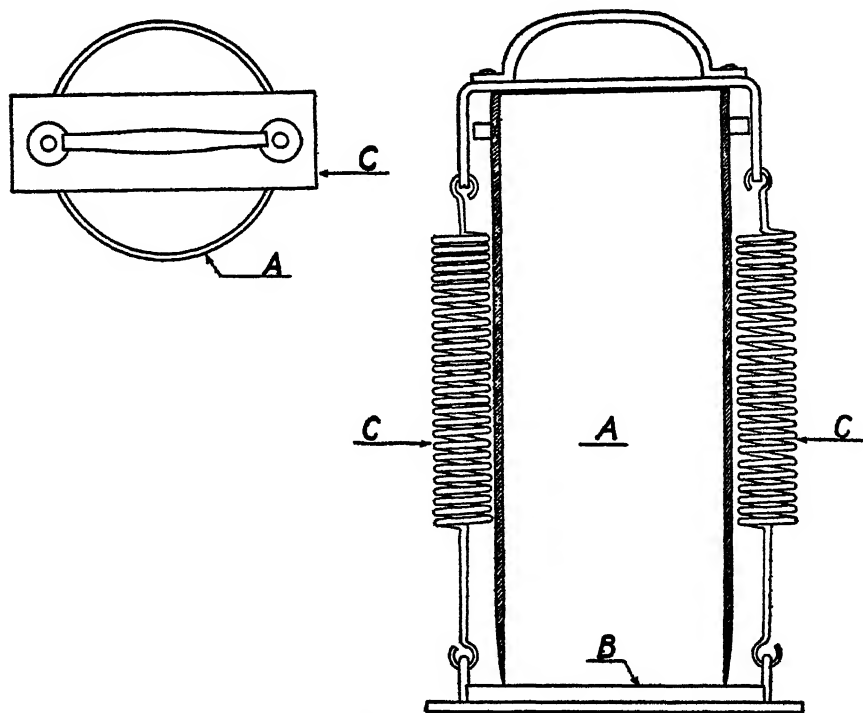


FIG. 2. APPARATUS FOR SAMPLING SOIL IN AN UNDISTURBED CONDITION  
Seen from above and in longitudinal section. Explanation in text.

#### PRACTICAL APPLICATIONS

##### *Aerobic soils*

On an experimental field of the polder "Urkerland," consisting of a well-aerated sandy clay, eight soil samples were taken in the cylinders shown in figure 2. In each cylinder two electrodes of platinized platinum were inserted to a depth of 10 cm. From eight additional soil samples taken from the same places, chloroformed 1:1 suspensions in water were prepared (the chloroform was added to prevent a negative drift due to bacterial activity). In table 3 the redox potentials measured on the eight spots *in situ* and in suspensions are compared.

These results are typical for well-aerated soils. Most of the potentials measured *in situ* were much higher than the potentials of the suspensions.

Potentials were also measured of suspensions of the same soil after the air had been removed by aeration with purified nitrogen. The following potentials were found in six chloroformed suspensions: -250, +28, -122, -122, -197, +4. Though the reproducibility of these measurements is far from ideal (probably because of an unequal removal of oxygen), it is evident that, even in this well-aerated soil, highly reducing conditions may be obtained solely by the removal of oxygen.

TABLE 3

*Redox potential measured on eight spots of an experimental field of the polder "Urkerland"*

On each spot the potential was measured *in situ* (with two platinized electrodes) and in a chloroformed 1:1 suspension (with one platinized electrode)—Eh in millivolts.

SAMPLE .....	1	2	3	4	5	6	7	8
Eh <i>in situ</i> .....	708	765	495	720	761	710	714	823
	708	731	596	766	783	659	719	802
Eh in suspension .....	605	608	595	555	575	583	583	59

TABLE 4

*Redox potential measured on eight spots of a field on the Isle of Schouwen 5 months after inundation*

On each spot the potential was measured *in situ* (with two platinized electrodes) and in a chloroformed 1:1 suspension (with one platinized electrode). Spots 1, 2, 3, and 4 were on a dry part of the field; spots 5, 6, 7, and 8 were on a somewhat wetter part of the field—Eh in millivolts.

SAMPLE .....	1	2	3	4	5	6	7	8
Eh <i>in situ</i> .....	676	529	715	685	557	645	602	449
	707	615	686	620	510	610	108	493
Eh in suspension .....	144	154	154	160	171	171	188	194

When the percentage of reducing substances is increased, the effect of small deficiencies in aeration may be very pronounced, though the potentials of a well-aerated soil may be as high as those of normal soils. This effect was observed during the measurement of the redox potential of a soil from the Isle of Schouwen that had been flooded with salt water during the war but had become dry again in the summer of 1945. In October 1945, eight samples were taken in cylinders, four from dry well-aerated soil on the higher part of a field between two drains and four from the lower, wetter part of the same field over a drain. From the same places aerobic, chloroformed 1:1 suspensions were also prepared. The potentials measured are summarized in table 4.

It is evident that the average redox potential of the wet spots is lower than the

average of the dry spots; and further, that in the soil suspensions the redox potential is far lower than that measured *in situ*. It appears that the difference between the potentials of the two groups of soils *in situ* is caused entirely by a difference in aeration, as in the suspensions the potentials at the spots over the drains are actually somewhat higher than the potentials at the spots between the drains. Our conclusion is that the redox potential of well-aerated soils is determined mainly by the degree of aeration and that the quality of reducing substances is important only in so far as it influences the effect of de-aeration.

### *Anaerobic soils*

Flooding of many parts of Holland with salt water during the war provided an excellent opportunity for a study of the redox potentials of highly reduced soils, especially on the Isle of Walcheren. On this island, which was subjected to the tidal movement of the sea water, thick layers of fresh sea silt became deposited in places, and, elsewhere on the same island, soil had been taken up by the water and redeposited at other localities ("removed soil"). Most of these newly deposited layers contained remarkably large quantities of sulfides, which gave them the well-known black color of reduced soils, while the underlaying original soil was, in the main, much lighter in color.

It appeared of interest to compare the sulfide concentration with the redox potential of the soil. The percentage of sulfides (monosulfides and polysulfides) was measured by a method<sup>2</sup> in which the soil is reduced with  $\text{HCl}$  and tin and the  $\text{H}_2\text{S}$  evolved is titrated iodometrically. For technical reasons, it was impossible to measure the redox potential in the field, and again measurements had to be made in cylinders. This offered some difficulties when applied to soils still under water. Some of the most interesting results are summarized in table 5.

From these observations the following conclusions may be drawn:

The lowest potentials observed in these highly reduced soils have the value of  $E_h = \pm -200$  to  $-250$  millivolts. It must be assumed that the value  $-250$  millivolts is the apparent reduction potential of certain highly reducing substances in the soil under strictly anaerobic conditions. This apparent reduction potential is very unstable, slight aeration being sufficient to give rise to higher potentials. These low potentials may be found in all kinds of soils, independent of the amount of sulfides, provided strictly anaerobic conditions exist. Of course, anaerobic conditions will be produced more rapidly, the higher the concentration of the sulfides. In practice, therefore, these low potentials can be most easily found in soils containing high quantities of sulfides. When strictly anaerobic conditions are produced by other factors, potentials of  $-250$  millivolts may be found even in soils containing no sulfides, as has been mentioned.

During the first weeks following removal of the overlying water, the soils are still very wet and poorly aerated. Then they show a fairly reproducible potential varying between the limits  $-50$  and  $+50$  millivolts. Potentials of this magnitude could be observed in all kinds of soils independent of the amount of sulfides and the amount of humus (grassland). The often astonishing reproducibility of these potentials (*in situ*) gives rise to the supposition that the soils contain a reversible well-poised redox system with  $E_o' \pm 0$  millivolts.

<sup>2</sup> To be described elsewhere.

TABLE 5

*Redox potentials of soil of the Isle of Walcheren measured while flooded with sea water and after being drained*

The redox potential was measured *in situ* on four spots with two platinized electrodes (in cylinders)

SOIL	TIME OF MEASUREMENT	RE- DUCED S	WATER CON- TENT	pH	REDOX POTENTIAL			
		per cent*	gm.†		1	2	3	4
Silt	While flooded	0.864	66.7		mv. -240 -219	mv. -56 -201	mv. -153 -201	mv. -45 -9
	Some weeks after draining				-25 -15	-19 -25	-28 -27	-45 -9
	2 months after draining				+98 -12	+114 -174	-207 -26	-20 -9
Silt	While flooded	0.315	50.1	7.98	-247 -229	+58 -176		
	2 months after draining (low and wet spot)				-14 -17	-20 +9	-15 -15	-24 -24
	2 months after draining (aerated spot)				+608 +110	+139 -124	+60 +574	+158 +296
Removed soil	3 weeks after draining	0.053	22.1		+6 -122	+50 -150	+18 +266	+28 -125
	3 months after draining		19.6	7.95	-116 -90	-181 -162	-177 -46	-261 +355
	6 months after draining		19.6	7.80	+564 +583	+402 +656	+766 +740	+73 -335
Grassland covered by silt layer	While flooded				-200 -152	-165 -228	-195 -173	-225 -132
	Some days after draining	0.077	41.9	8.15	+34 -26	+27 -35	-21 +13	-140 +80
	2 months after draining		29.3	5.40	+501 +513	+615 +418	+224 +544	+549 +608
Grassland not covered by silt layer	Some days after draining			8.15	+2 +18	-25 -13	-25 +10	-10 +1
	2 months after draining		25.6	5.80	+660 +672	+621 +615	+669 +709	+671 +625
Arable land covered by silt layer	Some days after draining	0.026	29.8	7.95	+23 +5	-72 -4	+50 -12	-24 -15
	2 months after draining		29.6	7.40	+23 +109	+46 +38	+100 +66	+74 +75

\* S in dry soil. † Per 100 gm. soil.



TABLE 5—Continued

SOIL	TIME OF MEASUREMENT	REDUCED S	WATER CONTENT	pH	REDOX POTENTIAL			
		per cent <sup>a</sup>	gm †		1 mv.	2 mv.	3 mv.	4 mv.
Arable land not covered by silt layer	While flooded			7.95	-111	-47 -21		
	Some days after draining			7.95	-90 +40	+36 +44	+30 +28	-9 +32
	2 months after draining		25.5	7.40	+629 +648	+398 +337	+392 +339	+387 +98
Arable land covered by removed soil	3 weeks after draining	0.024	19.5		+55 +93	-35 +66	-32 +85	+47 -105
	3 months after draining		17.1	7.17	+235 +592	+452 +618	+419 +606	+597 +401

\* S in dry soil. † Per 100 gm. soil.

During the further aeration and drying of these soils, the measurements *in situ* often cannot be readily reproduced. This is to be expected, since there is not uniform aeration throughout the soils. Sometimes potentials observed after some months of drying were lower than those observed immediately after the water was pumped out. This might have been due to aeration by the passage of the oxygen-containing water layers during the pumping out of the water. During the drying of the soils, lumps of clay are formed in which the diffusion of gaseous oxygen is difficult, and again anaerobic conditions develop.

It might be expected that the velocity of the aeration would depend on the concentration of the sulfides and other reducing substances. At first sight, the measurements seem to meet this expectation, since silts with the highest concentration of sulfides appear to be more gradually aerated than the original soils, and silt layers even seem to retard the aeration of the underlying soil. A close examination of the results, however, shows that the concentration of the reducing substances cannot have been the only factor governing the aeration of these soils. The slow aeration of the silt layers may have been caused mainly by the compact structure of these fresh deposits. In many instances, the upper layers of silt still were strongly reduced while the underlying soil was already fairly well aerated.

### Conclusions

The number of observations is much too small to give a good impression of the redox potentials of the soils studied. Because of the great variance between the measurements *in situ*, it would be necessary to make many more measurements on every type of soils than has so far been possible. When technical means are available for measuring the redox potential in the field, rather than in a limited number of cylinders, there will be no reason to restrict the number of measurements to eight. The measurements made do, however, provide some information about the factors which determine the oxidation-

reduction potential of a soil. It may be concluded that the main factor governing the redox potential of a soil is the degree of aeration, though of course the concentration of the reducing substances is highly important also. It is not surprising that most authors who have worked with suspensions of soil have concluded that the measurements of oxidation-reduction potentials fail to give any indication of the aerobic or anaerobic character of the soil. For example, Willis (5) has said: "...it does not seem possible to define the terms aerobic and anaerobic narrowly in terms of potential." On the other hand, measurements of the redox potential *in situ* give a reliable impression of the aeration level of the soil. The potentials then measured appear to be greatly influenced by the water level and by the structure of the soil. In suspensions, the potential is determined only by some chemical properties of the soil.

When the observations are converted to rH, the limits of the redox potentials in soil can be defined as  $rH = 40$  and  $rH = 7$ .

#### SUMMARY

Measurements of oxidation-reduction potentials of suspensions of a soil cannot give a true picture of the oxidation-reduction character of the soil. A true picture is possible only when the measurements are made *in situ* in the field.

Electrodes of platinized platinum give better results than electrodes of bright platinum, particularly in well-aerated soils.

The oxidation-reduction potentials of well-aerated soils will be determined primarily by oxygen. Consequently the potential measured at the electrode will be lower than the actual potential of the soil.

In more reduced soils, platinum electrodes will give more reliable results, because the concentration of soluble reversible redox-systems is increased.

A method of measuring the oxidation-reduction character of a soil *in situ* in the field is described.

Some applications of the method, particularly to soils that had been flooded with sea water, are described. It appears that the oxidation-reduction level of these soils was mainly determined by the aeration of the soil (water level, water content, structure of the soil), though the concentration of reducing substances was also very important.

When the redox potential of a soil is determined in the field, it is possible to define the aerobic or anaerobic character in terms of the potential.

The potentials observed in the soils studied varied between  $rH = 40$  and  $rH = 7$ .

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# A LABORATORY PROCEDURE FOR DETERMINING THE FIELD CAPACITY OF SOILS

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Field capacity has been described as the practical upper limit of soil moisture content found under field conditions in a soil having unobstructed subdrainage. It is therefore an important soil water storage characteristic and occupies a useful place in soil mapping and water utilization studies. The purpose of this paper is to describe a laboratory procedure for its determination.

The direct measurement of field capacity must be made in the field by a determination of the moisture content of freshly irrigated and gravity-drained soil (3). This determination is often impracticable, especially when a large area is being studied, when the terrain is rugged, or when water supply is limited. As a result, a number of investigators have studied relationships between field capacity and some characteristic of the soil readily determined in the laboratory. Thus Olmstead (7) irrigated soil columns 18 inches high and drained the excess water from them into dry soil beneath. He concluded that the average moisture content of the upper half of the drained soil column was a fair measure of its field capacity. Wilcox and Spilsbury (12) found that the field capacity of certain Canadian soils was closely related to the percentage of sand they contained. The most widely studied relationship has involved the moisture equivalent. Browning (1) and Harding (4) found moisture equivalent to be equal to field capacity at a value of about 21 per cent; they also found that the field capacity was greater than the moisture equivalent in soils of lower field capacity, whereas the reverse was true for soils with higher field capacity values. Veihmeyer and Hendrickson (11) found substantial agreement between the two values in the range between 12 per cent and 30 per cent. Mathews (6), Burr and Russel (2), and Work and Lewis (13) came to the conclusion that the field capacity was slightly less than the moisture equivalent in the soils they studied. Stoltenberg and Lauritzen (9) reported that the field capacity: moisture equivalent ratio varied from 0.74 to 1.24. The differences between these findings may be due to local soil conditions, to differences in technique used in the field capacity determination, or to some of the difficulties which Veihmeyer (10) and others have shown to be inherent in the centrifuge method of moisture equivalent determination.

<sup>1</sup> Forester, California Forest and Range Experiment Station, maintained by the Forest Service, U. S. Department of Agriculture, in cooperation with the University of California at Berkeley.

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In the present study a relationship was sought between the field capacities of a number of soils and the equilibrium moisture contents which they reached when drained on a porous ceramic cell under a constant moisture tension.

#### PROCEDURES AND RESULTS

Field capacities of the soils used in this study were determined by two methods. The first made use of data from a soil water utilization study conducted on the San Dimas Experimental Forest of the U. S. Forest Service, in the San Gabriel Mountains of southern California. Here repeated soil moisture samplings made on small field plots during five rainy seasons have provided a reliable measure of the field capacities of a number of upland residual soils. The second method involved the irrigation of field plots and the moisture determination of soils of these plots after drainage of the irrigation water had ceased. Some 30 soils were selected so as to cover a wide textural range. Some were cultivated alluvial soils on the north side of the San Gabriel Valley of southern California and some were brush covered residual soils in the adjacent mountains. In all these soils the water table was too far below the surface to affect the moisture content of the sampled block and, in all, subdrainage was unobstructed.

Sufficient water was ponded on a 4-foot by 4-foot irrigation check laid out on each of these soils to ensure moisture penetration at least 4 feet deep. Following the disappearance of water from the surface, the plots were covered with heavy canvas to minimize evaporation, and moisture samples were taken daily for a week through the first 2 feet of depth. In all cases the soil moisture was found to remain substantially constant after the first day of drainage, indicating that the field capacity had been reached within this time. Samples for laboratory study were chosen from those depths and plots showing the most consistent field capacity values through the sampling periods.

Approximately 120 samples were analyzed in the laboratory, including about 70 from the irrigated plots and 50 from those sampled periodically. They ranged in field capacity from 4 per cent to 32 per cent and represented a fair sampling of the well-drained soils found in the valleys and mountains of southern California.

Only soil material passing a  $\frac{1}{4}$ -inch mesh sieve was used in the laboratory part of this study because of the inaccuracies which result when analyses are made of small samples of soil containing larger gravel and rock particles. In order to make laboratory and field measurements comparable, the field capacity moisture content was calculated on the basis of soil material passing the  $\frac{1}{4}$ -inch sieve only, the assumption being that larger solid particles held an insignificant amount of water at this moisture content.

The moisture tension apparatus was similar in design to that described by Richards and Weaver (8) in their study of the relation of soil moisture to tension within the tension range of 0 to 1 atmosphere. A partly evacuated carboy was used in place of their hanging water column to maintain the several drainage tensions investigated in the preliminary studies, and an automatic vacuum control valve was used for the maintenance of the constant tension finally selected.

At the start of the study it was suspected that the field capacity moisture contents of all the soils collected might be duplicated when these soils were drained to moisture equilibrium under some constant tension value. This was in accord with the suggestion of Lyon and Buckman (5, p. 156) that a tension of  $\frac{1}{2}$  atmosphere (pF 2.7) is representative of the moisture tension at field capacity. To test this possibility, a number of soils were saturated and then drained under moisture tensions ranging from 2 to 50 cm. of mercury (0.03 to 0.66 atmosphere). As is shown in figure 1, the moisture tension corresponding to field capacity is

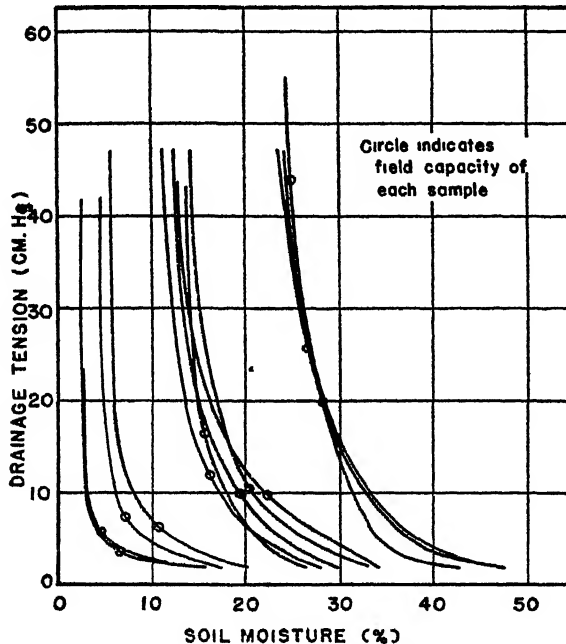


FIG. 1. RELATION BETWEEN FIELD CAPACITY MOISTURE AND MOISTURE TENSION OF LABORATORY-DRAINED SOIL BLOCKS

The field capacity value is shown on each moisture-tension curve

not constant but increases as the field capacity increases. Whether this relationship would also be found in soils *in situ* or whether it is a result of the granulating treatment the soils received in sampling and in the laboratory has not been determined. Regardless of its cause, however, these results make it evident that no single moisture tension will bring all soils to their field capacities under laboratory conditions.

Failure to find a single tension under which all soils could be drained to their field capacities led to use of an arbitrarily chosen constant drainage tension for all soils, and then to determination, for these soils, of the relationship existing between field capacity and the moisture retained against this tension. Richards and Weaver (8) had found that the soil moisture retained against a tension of

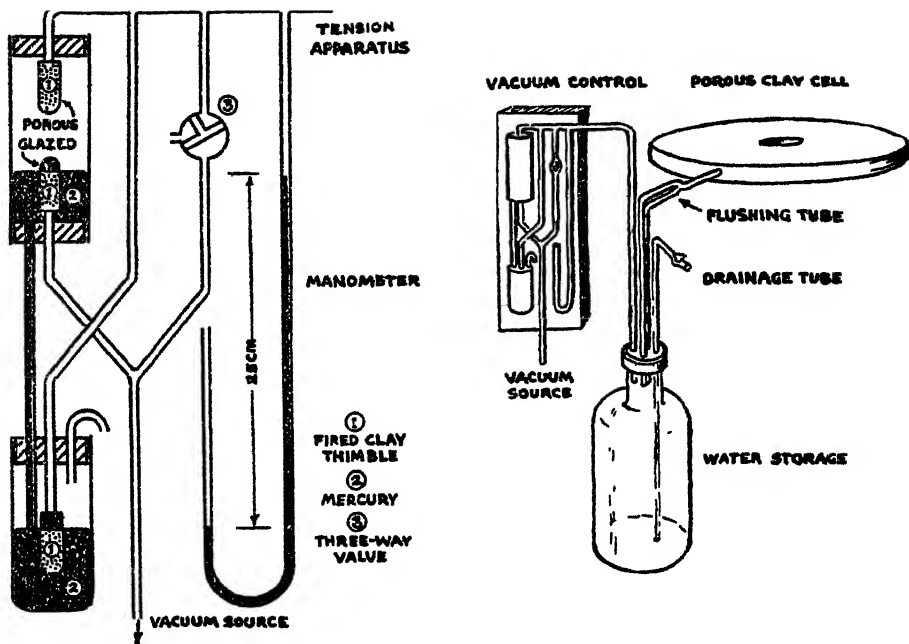


FIG. 2. CONSTANT-TENSION DRAINAGE APPARATUS AND VACUUM CONTROL VALVE USED FOR DETERMINING THE  $\frac{1}{3}$ -ATMOSPHERE SOIL MOISTURE PERCENTAGE

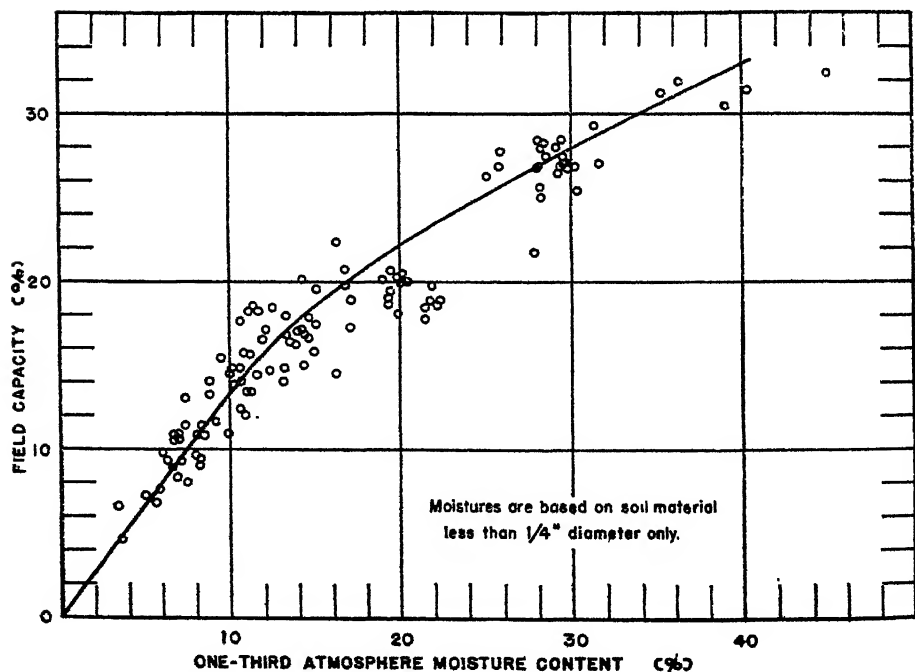


FIG. 3. RELATION BETWEEN FIELD CAPACITY OF SOIL AND ITS  $\frac{1}{3}$ -ATMOSPHERE MOISTURE PERCENTAGE

25 cm. of mercury ( $\frac{1}{3}$  atmosphere) closely approximated the moisture equivalent. This seemed sufficient reason for selecting 25 cm. of mercury as the drainage tension to be used in the present study.

The laboratory apparatus was modified by eliminating the evacuated carboy and inserting between the drainage bottle and the high vacuum line an automatic vacuum control valve designed to maintain the water in the porous ceramic cell at a tension of 25 cm. of mercury. The tension equipment is illustrated in figure 2.

A consistent relationship was found to exist between the moisture retained against 25 cm. mercury tension and field capacity. It will be noted in figure 3, which represents this relationship, that the curve fitted to the data shows field capacity and  $\frac{1}{3}$ -atmosphere moisture percentage to be equal at about 25 per cent. At lower values the field capacity is greater than the  $\frac{1}{3}$ -atmosphere percentage, and at higher values it is less. This is in substantial agreement with the relationships between field capacity and moisture equivalent discussed earlier, although agreement is more in principle than in fact.

On the basis of this study the  $\frac{1}{3}$ -atmosphere moisture percentage is proposed as a laboratory measure which can be used for the indirect determination of field capacity. Two precautions in the general use of figure 3 must be mentioned. First, the curve is based upon the data obtained from soils collected within a limited area, and the possibility exists that soils developed under other climatic, geologic, or topographic conditions may not exhibit the same relationship. It is suggested that soils in other regions be studied by the method described here to test the wider applicability of the present results. Second, figure 3 relates specifically to young or immaturely developed, free-draining soils in which the water table is so far below the layer under consideration that it exerts no influence upon the rate or completeness of drainage of that layer. The curve would not be expected to hold for soils in which the water table is only a few feet below the surface, or those in which drainage is impeded by a horizon of very low permeability.

#### METHOD OF DETERMINING THE $\frac{1}{3}$ -ATMOSPHERE MOISTURE PERCENTAGE

The sieved soils are poured into 1-inch-long sections of 1-inch-diameter seamless brass tubing resting on the ceramic tension cell, and are tamped lightly. The cell surface is then flooded, permitting the soil blocks to become saturated from below. Saturation of soils that resist initial wetting or of those containing considerable organic or inorganic colloidal material may require several hours of soaking. During this time a valve on the vacuum line is kept closed to prevent absorption of water into the tension cell. When saturation is complete, surplus water is pipetted from the surface of the cell and the vacuum valve is opened, initiating drainage of the samples under the  $\frac{1}{3}$ -atmosphere tension. Three hours' drainage has been found adequate for all soils studied. Evaporation is prevented by placing a sheet-metal cover over the cell and the samples. At the end of the drainage period the moisture content of each soil sample is determined.

If the soils analyzed contain, in their field condition, considerable rock ma-



terial greater than  $\frac{1}{4}$ -inch in diameter, and if the *in situ* field capacity is to be calculated, it is necessary to correct the laboratory-determined field capacity for the weight of particles that do not pass the  $\frac{1}{4}$ -inch sieve. This is done with the assumption that the larger particles contain a negligible amount of water at field capacity. The *in situ* field capacity is then calculated by dividing the laboratory field capacity moisture percentage by 100 plus the percentage of soil material retained by the  $\frac{1}{4}$ -inch sieve. The percentage of soil retained must be calculated on the basis of the dry weight of the soil passing the sieve.

#### SUMMARY

The usefulness of the field moisture holding capacity as a soil characteristic coupled with the difficulty of its direct determination has led to the search for unique relationships which may exist between this value and some soil characteristic which can be readily measured in the laboratory. Such laboratory measurements studied in the past have included the moisture equivalent, mechanical analysis, and moisture content of short soil columns drained into air-dry soil beneath.

In the present study it was found that if small soil blocks were drained on a porous ceramic cell under a moisture tension of  $\frac{1}{3}$  atmosphere the moisture retained in the blocks could be related empirically to the field capacity of the same soils determined under natural field conditions.

A satisfactory degree of consistency was observed in the relationship between  $\frac{1}{3}$ -atmosphere moisture percentage and field capacity. It is suggested that the procedure described may provide a convenient and rapid way of making an indirect determination of field capacity.

Details of the design of the ceramic cell and moisture tension control equipment are given.

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# A NEW METHOD FOR ESTIMATING THE SURFACE OF LIMING MATERIALS AND OTHER INSOLUBLE CALCIUM COMPOUNDS

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Extensive work reported by Bear and Allen (1), Salter and Schollenberger (3, 4), and Morgan and Salter (2) has shown that the rate of reaction of calcium carbonate in an acid soil or in any dilute acid medium is a function of the surface exposed. A screen test is the common method of estimating the surface. The screens employed are rarely finer than 100-mesh, and it is a common practice to estimate the degree of fineness solely, or at least principally, on the basis of the percentage of 100-mesh material.

That this is not always a true estimate is illustrated by the following experiment. In November, 1944, as a part of an experiment to compare a new furnace

TABLE 1  
*Screen tests of natural and synthetic limestone meals*

	8-MESH	20-MESH	60-MESH	100-MESH
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Natural limestone meal.....	99.7	73.4	45.2	35.6
Synthetic limestone meal.....	100.0	99.0	49.0	27.0

TABLE 2  
*Effect of natural and synthetic limestone meals on pH of soil*

	pH* AT END OF		
	3 months	6 months	1 year
Natural limestone meal.....	6.03	5.91	6.14
Synthetic limestone meal.....	6.09	6.19	6.45

\* Each figure represents the average of three pots.

slag product with a limestone meal, the two materials were mixed with an acid soil in pots, which were then incubated with periodic wetting for months. Since the slag and the limestone meal showed a different size distribution by screen test, the comparison was carried out in two ways: First, the materials were compared in their natural states, and second, the limestone was screened into narrow range separates, which were then compounded so that the synthetic product had the same screen test as the slag. The screen tests of these two limestones are shown in table 1. As can be seen, only 27 per cent of the synthetic limestone was 100-mesh material, as compared to 35.6 per cent of the natural material.

The reaction of soil treated with equal weights of these two materials was determined at the end of 3 months, 6 months, and 1 year, with results shown in table 2. These data would seem to prove that the synthetic material had the greater reacting surface. A screen test, therefore, may often be misleading.

Accordingly a method was devised to measure the relative surface of a unit mass as a key to value in liming materials.

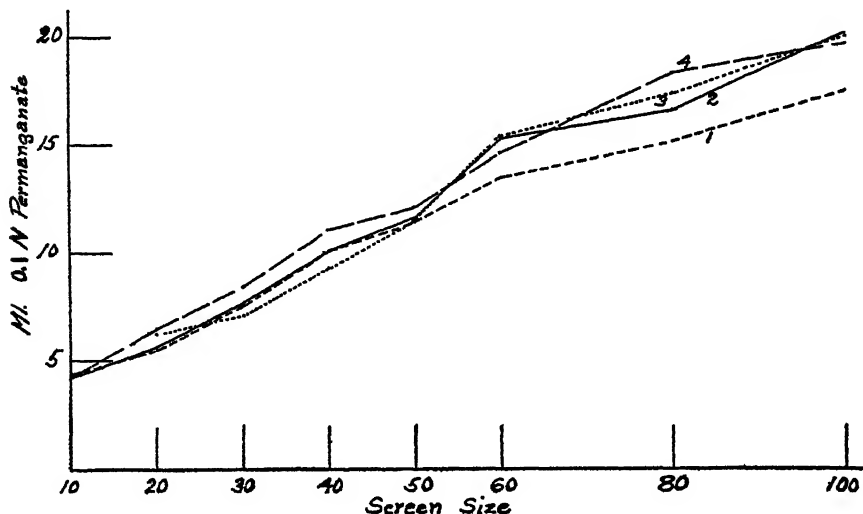


FIG. 1. RELATION OF TITRATION FIGURES TO FINENESS OF SEPARATES OF FOUR LIMESTONES

No.	Per Cent Ca	Per Cent Mg	Total Neutralizing Power	Source
1	32.4	4.63	100.0	Spore
2	21.8	13.17	108.4	Carey
3	34.1	4.55	104.0	Marion
4	32.2	5.21	101.9	Marblehead

#### THE NEW METHOD

The method is based on the fact that calcium oxalate is insoluble and on the hypothesis that if a mass of calcium carbonate were treated with oxalic acid a film of calcium oxalate would be formed on the surface of each particle, after which any reaction would be stopped or materially slowed down.

As a first step, screen separates of several limestones were prepared and each was thoroughly washed to remove all adhering dust. These separates were <8->20, <20->30, <30->40, <40->50, <50->60, <60->80, <80->100, <100->150. Their relative surfaces were determined by the following technique:

Weigh out 1 gm. limestone into an Erlenmeyer flask of about 300-cc. capacity. Treat with 5 cc. saturated  $(\text{COOH})_2$  and allow to stand  $1\frac{1}{2}$  hours. Transfer sample to filter, filter off excess  $(\text{COOH})_2$ , and wash thoroughly with hot water. Replace Erlenmeyer flask under

funnel and dissolve  $(\text{COO})_2\text{Ca}$  with hot dilute (1:4)  $\text{H}_2\text{SO}_4$ . (Three treatments of 2 cc. each, washing with hot water after each treatment, until effervescence stops suffices). Add 5 cc. concentrated  $\text{H}_2\text{SO}_4$  to filtrate and titrate with 0.1 *N* potassium permanganate.

Figure 1 shows the data for four limestones which varied widely in chemical composition. The significant feature is that the data plot a straight line for all materials, showing that the titration figure is directly proportional to the fineness.

#### PRACTICAL USE OF NEW METHOD

A large number of limestone products have been examined by this procedure. Some of the results, shown in table 3, indicate how this method can be used in lieu of a screen test or to supplement it in studying a liming material.

TABLE 3

*Comparison of screen tests and relative surface measurements of pairs of liming materials*

SAMPLES*	SCREEN TEST				0.1 <i>N</i> PERMANGANATE TITRATION	0.1 <i>N</i> PERMAN- GANATE TITRATION ON <150-MESH
	8-mesh	20-mesh	60-mesh	100-mesh		
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>cc.</i>	<i>cc.</i>
A	99	92	84.4	73.4	50.0	78.4
B	100	98.5	95.0	83.0	35.5	49.5
C	100	100	95	74	32.2	51.2
D	99.6	92.5	68.7	50.2	34.5	65.7
Slag	100	99	49	27	23.3	74
Limestone	100	99	49	27	24.0	70

\* See text for description of materials.

First a comparison was made between two materials of similar screen test. Material "A" was separated from glass sand by an air blast. Material "B" is a sludge washed from flux stone with water. Judged by the screen test, sample "B" would be considered the finer, but the reverse is shown by titration. The explanation is to be found in the fact that the <150-mesh material of the air-separated material is much finer than that of the water-separated material.

Another pair of materials, "C" and "D," were next compared. Material "C" is sold in sacks, and its screen test indicates a very fine high-calcium material. Material "D," sold in bulk, is a dolomite, which is classed as a No. 10 meal and retails at about half the price of the sacked material. Here again, in sample "D" the extreme fineness of the portion beyond the range of ordinary screen test more than compensates for the lower percentage of 100-mesh material.

That the method is adaptable to furnace slag is shown by comparison of the titration figures for a ground air-cooled slag with a limestone of the same screen test.

Some preliminary work has been done to investigate the adaptability of the

method for use with other relatively insoluble calcium compounds used in agriculture. For this comparison <80->100-mesh materials were separated and washed free of dust. The results were as follows:

MATERIAL	0.1 N PERMANGANATE
	TITRATION FOR 1 GM. CC.
Raw rock phosphate.....	12.3
Gypsum.....	34.1
Calcium carbonate.....	11.9
Air-cooled slag.....	22.6

A microscopic examination of these separates showed the raw rock phosphate and the calcium to be of fairly regular shape, roughly cubes. The slag was less regular in shape, and the particles were pitted. The gypsum was about 5 per cent crystalline. The crystals were flat plates; the rest was amorphous and of very irregular shape. Doubtless, both the slag and the gypsum had a greater surface per unit mass, because of the irregular shape, than did the more regular cuboid particles of raw rock phosphate and calcium carbonate. Also it is possible that the high titration of the gypsum was caused in part by its greater relative solubility. It seems quite possible, however, that the method could be used for comparing the surfaces of different samples of gypsum.

In an attempt to evaluate the permanganate titration in terms of square centimeters, the surfaces of several crystals of Iceland spar were carefully measured. Some of these were cubical and others were flat plates. For the cubical pieces, it was found that each cubic centimeter of 0.1 N permanganate titration represented a surface of 8 sq. cm. For the flat pieces, the average was about 12 sq. cm. This difference is thought to be caused by differential smoothness of the different crystal faces, or possibly by different orientation of the  $\text{CaCO}_3$  molecules on the different faces.

In a further study of the effectiveness of the synthetic (furnace slag) material and the natural limestone meal used in the 1944 pot experiment, two limestone products were prepared, one having the same screen test as the natural limestone and the other having the same screen test as the synthetic material (see table 1). Relative surface measurements by the new method, in terms of 0.1 N permanganate per gram of limestone, were as follows: natural size frequency, 23 cc.; synthetic size frequency, 24 cc. Since these products were cubical, the absolute surface (relative surface  $\times$  8) was 184 sq. cm. for the former, and 192 sq. cm. for the latter. These data agree well with the effect on the soil reaction in indicating that the synthetic size frequency has a greater surface than the natural size frequency.

#### SUMMARY

A method for measuring the relative surface of insoluble calcium salts is described. The method is based on the fact that calcium oxalate is insoluble and when an insoluble calcium salt is treated with oxalic acid a coating of insoluble calcium oxalate is formed on the surface. By washing the sample free of excess oxalic acid, decomposing the calcium oxalate with sulfuric acid, and

titrating the liberated oxalic acid with standard potassium permanganate, the relative surface can be measured.

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# A NEW ELECTRICAL RESISTANCE THERMOMETER FOR SOILS<sup>1</sup>

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Though thermometers abound, both in number and type, it is generally agreed that inexpensive instruments which are suitable and practical for accurately measuring soil temperature under field conditions are scarce. This was forcibly brought to light when in 1940 a thermometer was required to accompany the electrical resistance plaster of paris block method for making a continuous measurement of soil moisture under field conditions.<sup>2</sup> Since the electrical resistance of the gypsum moisture block is influenced by temperature, a suitable soil thermometer was required for making temperature corrections on the block resistance. Various types of thermometers were investigated. These included many kinds of mercury, dial, and bimetallic thermometers. None of these proved entirely satisfactory, because they were fragile, unstable and therefore unreliable, unsuitable for deep depths, or not sufficiently sensitive. Most of these objections could be overcome by using metallic electrical resistance thermometers, but such thermometers involve the use of a potentiometer. The inclusion of a potentiometer in a field kit, in addition to the Wheatstone bridge, was considered impracticable, not only because of the greater expense but also because of the inconvenience of handling and manipulating two complicated instruments. A more practical solution was therefore desired in the form of an electrical resistance thermometer adapted to the range of the already required bridge which would thus serve to measure both temperature and soil moisture.

In this paper are presented details concerning the design, construction, and characteristics of such an electrical resistance thermometer.

## PRINCIPLE OF THERMOMETER

This new thermometer is based upon the fundamental principle that the electrical resistance of inorganic liquids and of organic liquids containing electrolytes increases with decreases in temperature.

The liquids that were finally selected and used in this thermometer were "Prestone" (ethylene glycol to which certain stabilizing compounds have been added) and a mixture of "Prestone" and glycerine. In pure form these organic liquids are supposedly nonconductors or poor conductors of electricity, but in commercial form they contain traces of electrolytes which impart a certain degree of conductivity and make their resistance highly sensitive to changes of temperature.

<sup>1</sup> Journal Article No. 836, New Series (N. S.), from the Michigan Agricultural Experiment Station.

<sup>2</sup> Bouyoucos, G. J., and Mick, A. H. 1940 An electrical resistance method for the continuous measurement of soil moisture under field conditions. Mich. Agr. Exp. Sta. Tech. Bul. 172.

The resistance of this thermometer is measured by a specially designed portable Wheatstone bridge (fig. 1) which measures from 0 to 5,000,000 ohms with a high degree of sensitivity.

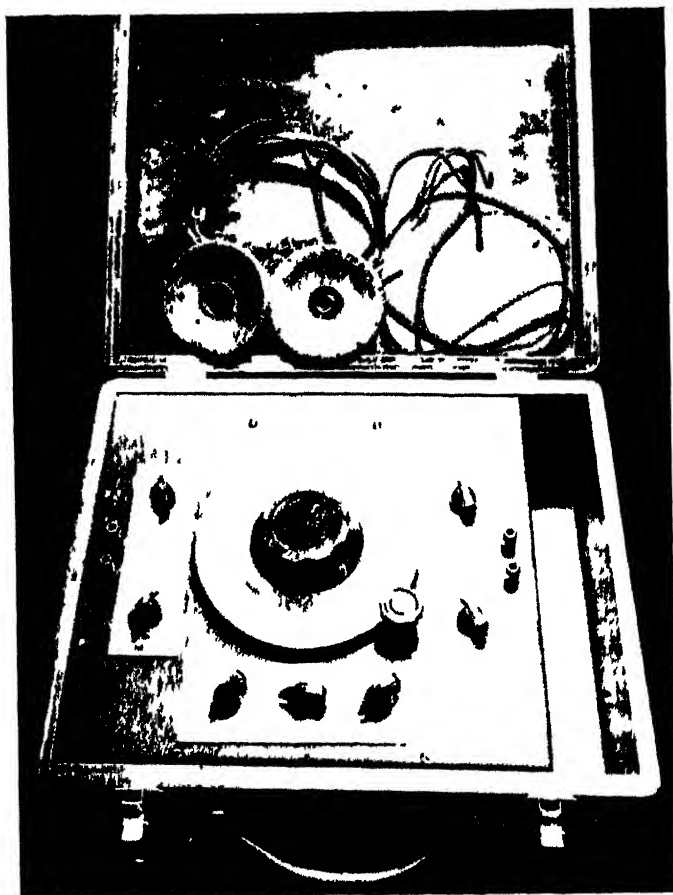


FIG. 1 SPECIAL BRIDGE

#### CONSTRUCTION OF THERMOMETER

Construction of this liquid electrical resistance thermometer is schematically shown in figure 2. Parallel platinum electrodes are sealed in a small thin-walled glass vial of special composition designated as "G 81." The glass walls are 0.5 mm. thick to facilitate thermal conduction. The vials were fashioned by a glass blower who first sealed the electrodes to the shoulder, then adjusted them inside the tube, and finally sealed the bottom. Liquid was introduced by means of a vacuum pump connected through a three-way stopcock to the narrow upper tube. This narrow tube was then sealed, leaving sufficient space above the liquid to permit expansion. Wire leads were soldered to the platinum electrodes,

and the joints were then covered with an insulation consisting of hot asphalt-compound and talcum. This insulation is characterized by considerable hardness and strength without brittleness within soil temperature ranges. In its finished form the thermometer is shown in figure 3.

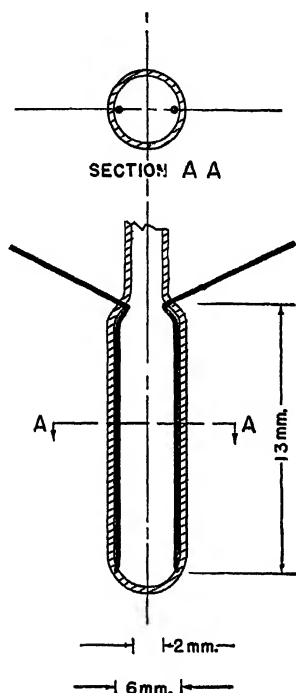


FIG. 2. BASIC CONSTRUCTION OF ELECTRICAL RESISTANCE THERMOMETER



FIG. 3. ELECTRICAL RESISTANCE THERMOMETER IN FINISHED FORM

#### BASIC STUDIES ON THERMOMETER

Two different types of thermometers were made: type 1, which uses "Prestone" entirely and is intended for measuring the lower range of temperature, especially from  $-20^{\circ}$  to about  $100^{\circ}\text{F.}$ ; and type 2, which uses a mixture composed of two parts of glycerine and one part of "Prestone" and is intended for measuring the higher temperatures, especially those from about  $32^{\circ}$  to about  $135^{\circ}\text{F.}$  Neither of these thermometers is intended for very high temperatures; both are primarily for the temperatures that prevail in soil.

When the thermometers were first prepared, it was noticed that the electrical resistance of both types decreased slightly with the lapse of time at any given temperature. It is thought that this decrease in resistance is due to the solubility of the glass and to a possible change in the liquid. After a time this change ceased and an equilibrium was reached. It was found, however, that the attainment of this equilibrium could be hastened by heating the sealed thermometer bulbs, with the liquid in them, in an oven at  $220^{\circ}\text{F.}$  for about 10 days.

Thermometers so treated have remained constant in their calibration for almost 2 years, the longest period of study.

Both types of thermometers are very sensitive to temperature changes and attain a final equilibrium in less than 2 minutes, or at about the same rate as in mercury thermometers. Faster attainment of equilibrium in the electrical thermometers is prevented probably by the insulation which covers part of the thermometer at the shoulder.

Thus far the electrical resistance thermometer has been made entirely by hand. In order to standardize the construction so that all thermometers within the type will be alike, two conditions must be satisfied: first, the electrodes must be exactly the same distance apart, and second, they must be of exactly the same length. Of the two factors, the length seems to be the more important because the surface of the electrodes is affected. It is rather difficult to meet these conditions and attain a very high percentage of agreement when the thermometers are made manually. The degree of standardization thus far attained, however, is revealed by the following figures. Of 100 hand-constructed thermometers, 38 gave identical resistance readings at any selected temperature, 42 varied within 1°F. at any given resistance, and the remainder agreed within 2.5°F. It is possible that an experienced glass blower could manufacture similar instruments with a much higher degree of agreement. Variation in the construction of the thermometers is not a serious handicap, however, because the resistance-temperature characteristics are of a nature (as will later be shown) to permit ready application of correction factors.

Various tests have failed to show that any significant electrolysis and polarization occur in the liquid when the thermometer is left connected to the current in the Wheatstone bridge. Thermometers that were left connected to the current in the Wheatstone bridge for 4 days gave the same calibration as before, showing that no change was induced in the liquid by the current.

The thermometer is characterized by capacitance factors which increase with the length of the wire leads. Errors induced by capacitance factors were satisfactorily eliminated by separating the leads and employing moisture-proof insulation.

Though the type 1 thermometer is capable of measuring soil temperatures as low as -25°F. it was found that if the Wheatstone bridge is exposed to this low temperature its batteries become weak and the signal consequently weakens.

#### CALIBRATION OF THERMOMETER

The finished thermometer, as shown in figure 3, was calibrated so that its electrical resistance would read directly in degrees Fahrenheit. This was done by placing the bulb of the thermometer in a temperature bath containing water, or a mixture of water-ice-salt. The bath was well insulated, and it was possible to maintain a constant temperature at any given point for a reasonable time. The temperature was manually controlled and was measured by a specially made mercury thermometer with a long stem. The electrical resistance was read by the special Wheatstone bridge shown in figure 1.

The calibration results for the type 1 thermometer and those for the type 2 thermometer show that the electrical resistance of the thermometers is very sensitive to temperature changes. This is especially true in the lower temperature range. At about 40°F., for example, type 2 thermometer gives a resistance

TABLE 1

*Standard data for converting electrical resistance into temperature for type 1 thermometer ("Prestone")*

TEMPERATURE	RESISTANCE	TEMPERATURE	RESISTANCE	TEMPERATURE	RESISTANCE
°F.	ohms	°F.	ohms	°F.	ohms
95	34,300	63	65,600	31	152,000
94	34,900	62	67,000	30	157,000
93	35,500	61	68,500	29	162,500
92	36,100	60	70,100	28	168,000
91	36,800	59	71,700	27	173,500
90	37,500	58	73,300	26	179,500
89	38,300	57	75,000	25	185,500
88	39,100	56	76,800	24	192,000
87	39,800	55	78,700	23	198,500
86	40,500	54	80,700	22	205,000
85	41,200	53	82,800	21	211,500
84	41,900	52	84,900	20	218,000
83	42,700	51	87,000	19	224,500
82	43,500	50	89,200	18	231,000
81	44,300	49	91,400	17	238,000
80	45,100	48	93,700	16	245,500
79	45,900	47	96,000	15	253,000
78	46,800	46	98,300	14	261,500
77	47,700	45	101,000	13	270,500
76	48,700	44	104,000	12	280,000
75	49,800	43	107,000	11	289,500
74	51,000	42	110,000	10	299,500
73	52,200	41	113,100	9	310,000
72	53,400	40	116,300	8	321,000
71	54,600	39	119,500	7	333,000
70	55,900	38	123,000	6	346,500
69	57,200	37	126,500	5	360,000
68	58,500	36	130,300	4	374,000
67	59,800	35	134,200	3	388,500
66	61,200	34	138,100	2	403,500
65	62,600	33	142,200	1	420,000
64	64,200	32	147,000	0	438,000
				-1	460,000

change of about 50,000 ohms for 1° change of temperature; at approximately 75°F. it gives a resistance change of about 8,000 ohms for 1° change of temperature. Obviously, this ratio of electrical resistance to temperature change imparts to the thermometers a high degree of sensitivity.

It should be possible to construct a meter with a temperature scale on which to

read directly the temperature of the electrical resistance thermometers. Meanwhile, the temperature of these thermometers is being read on the Wheatstone bridge.

TABLE 2

*Standard data for converting electrical resistance into temperature for type 2 thermometer ("Prestone"-glycerine)*

TEMPERATURE	RESISTANCE	TEMPERATURE	RESISTANCE	TEMPERATURE	RESISTANCE
<sup>°</sup> F.	ohms	<sup>°</sup> F.	ohms	<sup>°</sup> F.	ohms
134	54,500	100	119,000	66	351,000
133	55,700	99	122,000	65	363,000
132	56,900	98	126,000	64	377,000
131	58,100	97	130,000	63	392,000
130	59,300	96	134,000	62	407,000
129	60,600	95	138,000	61	423,000
128	62,000	94	142,000	60	440,000
127	63,500	93	146,000	59	458,000
126	65,500	92	150,000	58	477,000
125	67,000	91	155,000	57	496,000
124	68,500	90	160,000	56	515,000
123	70,000	89	165,000	55	536,000
122	71,500	88	170,000	54	557,000
121	73,000	87	176,000	53	578,000
120	74,500	86	182,000	52	600,000
119	76,100	85	188,000	51	623,000
118	77,700	84	194,000	50	648,000
117	79,300	83	200,000	49	675,000
116	80,900	82	206,000	48	704,000
115	82,600	81	212,000	47	734,000
114	84,300	80	218,000	46	766,000
113	86,000	79	225,000	45	800,000
112	88,000	78	232,000	44	836,000
111	90,000	77	240,000	43	872,000
110	92,200	76	248,000	42	915,000
109	94,500	75	257,000	41	958,000
108	97,000	74	266,000	40	1,010,000
107	99,500	73	275,000	39	1,065,000
106	102,000	72	284,000	38	1,125,000
105	105,000	71	294,000	37	1,190,000
104	107,000	70	304,000	36	1,270,000
103	110,000	69	315,000	35	1,365,000
102	113,000	68	327,000	34	1,480,000
101	116,000	67	339,000	33	1,640,000
				32	1,900,000

To facilitate the conversion of the electrical resistance of the thermometers into degrees F. temperature, tables 1 and 2 have been prepared. Table 1 is for type 1 thermometer and table 2 for type 2. These tables constitute the standard basis for converting the electrical resistance readings of all thermometers of each type into degrees F. temperature. By referring any ohms resistance reading

to table 1 for type 1 thermometer, or to table 2 for type 2 thermometer, the temperature in degrees F. is immediately obtained. The tables are scaled into 1°F. divisions, but a small fraction of 1° can be easily estimated, since the resistance value per degree is comparatively large in type 1 thermometer when used at lower temperatures, and in type 2 thermometer when used at higher temperatures.

Tables 1 and 2 not only constitute the standard basis for converting the electrical resistance reading of all thermometers of the two types directly into degrees F. but will also serve as a standard for calibrating all the thermometers in each type to the same standard basis.

To calibrate all the thermometers so they will all read alike within their type, the following rapid and simple procedure is followed. The electrical resistance of an unknown thermometer is determined at a definite temperature in water, preferably at 75°F. This electrical resistance reading is referred to the standard thermometer at the same temperature in table 1 if the thermometer is type 1 ("Prestone"), table 2 if the thermometer is type 2 ("Prestone"-glycerine). If the electrical resistance of the unknown thermometer is greater than that of the standard thermometer, the difference is subtracted from the entire scale of the unknown thermometer, and that converts the reading of the unknown thermometer to the same standard basis as the standard thermometer. Conversely, if the electrical resistance reading of the unknown thermometer is less than that of the standard thermometer the difference is added to the entire scale of the unknown thermometer. Thus, by taking only a single temperature reading of the unknown thermometer, its entire scale is readily reduced to that of the standard calibrated thermometer shown in either table 1 or table 2.

This simple and rapid method of calibration is sound and valid because it was found experimentally that the electrical resistance differences in any two thermometers ran in virtually the same degree throughout the entire scale of the thermometers. For example, if the unknown thermometer varied from the standard thermometer by 5,000 ohms at 75°F., this difference remained virtually constant throughout the entire scale of the thermometers. This was true with both types of thermometers.

#### SUMMARY

Two types of liquid electrical resistance thermometer have been developed for measuring soil temperature under field conditions. Type 1 measures temperature from about -20° to about 100°F. Type 2 measures temperature from about 32° to about 135°F. In type 1 the liquid is entirely "Prestone." In type 2 the liquid is a mixture of "Prestone" and glycerine.

The liquid is contained in a glass vial fitted with platinum electrodes. The electrodes are connected to wire leads of any desired length, and the joints are permanently insulated with a special compound.

The electrical resistance of this thermometer is measured by the special soil moisture Wheatstone bridge, having a range from 0 to 5,000,000 ohms, which has been used in connection with the electrical resistance-plaster of paris block



method for making a continuous measurement of soil moisture under field conditions.

This new liquid electrical resistance thermometer is very sensitive to temperature changes and gives a high value of resistance for every 1°F. change of temperature. This is especially true at the lower range of temperature. At a temperature of around 40°F., for example, type 2 thermometer gives a resistance change of about 50,000 ohms for 1° change of temperature. At a temperature of around 75°F it gives a resistance change of about 8,000 ohms for 1° change of temperature. This high ratio of electrical resistance to temperature change imparts to the thermometer a high degree of accuracy.

The thermometers thus far used have been made only manually. In a set of 100, 38 per cent agreed exactly, the other 62 per cent varied by about 0.2° to 2.5°F. A rapid and simple procedure is offered to reduce all thermometers to the same standard basis. This is accomplished by taking a single temperature reading of the unknown thermometer and applying the variation from the standard temperature table to the entire scale of the unknown thermometer.

The thermometer is simple, convenient, and reliable for measuring the soil temperature at various depths.

# CHARACTERIZATION OF THE STABILITY OF SOIL AGGREGATES<sup>1</sup>

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The importance of the structural condition of the soil in relation to soil and water conservation and to crop growth is generally recognized. The specific characteristics of the most satisfactory structural condition for a given combination of soil conditions and plant requirements have yet to be established. One feature that is common to all desirable soil structures is water stability. It is apparent that only those structural units that resist disintegration when subjected to an excess of water are of significance under field conditions. Water stability is a relative quantity, however, and comparisons between soils can be made only in terms of measurements made under certain arbitrary but well-defined and controlled experimental conditions.

The most common techniques now used for characterizing the structural condition of soils involve the mechanical agitation of the sample in water at an arbitrary rate and for an arbitrary length of time. The fractional part of the original sample remaining in one or more size classes is then determined and used to describe the structural condition of the initial sample. In most cases measurements of this kind are made at only one arbitrarily selected intensity of agitation with the result that the data obtained allow comparisons to be made at a single point on the time *vs.* aggregate stability curve. When soils are compared on the basis of data obtained in this manner, conclusions relative to the stability of the aggregates may be quite different from those that would have been drawn if a different intensity of agitation had been used. It is obviously impractical to attempt to measure aggregate stability at all the possible intensities of agitation. A more satisfactory solution lies in attempting to specify analytically the relation between aggregate stability and the intensity of agitation. The following experiments were conducted in an attempt to develop a procedure suitable for characterizing this relation.

## MATERIALS AND METHODS

Four Iowa soils—Muscatine, Marshall, Knox, and Clinton silt loams—were used in these experiments. They are all loess-derived. The Muscatine, Marshall, and Knox silt loams have developed under prairie vegetation, whereas the Clinton has developed under deciduous forest. Air-dry samples taken from the 0-6-inch depth from each of the four soils were used. Since the objective of these experiments was to study the stability rather than the size distribution of

<sup>1</sup> Journal paper J-870 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 739.

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the aggregates and since the size of the sample used in the determination was so small that adequate sampling of an ungraded mixture of aggregate sizes was very difficult, all measurements reported here were made on aggregates of the 4.7- to 2.0-mm. size class. These were obtained from the whole soils by dry sieving, using a 4- and 9-mesh screen for the upper and lower size limits respectively.

The apparatus used in this investigation consists of six 2-inch brass sieves having 0.25-mm. openings. These sieves were oscillated vertically in water at the rate of 38  $1\frac{1}{2}$ -inch strokes per minute. To determine the water stability, 5 gm. of the previously graded aggregates were placed in each of the sieves and lowered into the water reservoir for a specified period of presoaking. Following this preliminary treatment, the samples were oscillated for the necessary time, after which the sieves were removed from the apparatus, inverted in small evaporating dishes, and washed free of the stable aggregates by a jet of water. The excess water was decanted from the evaporating dishes, which were then placed in the oven at 110° C. When thoroughly dried, the samples were removed from the oven and weighed, and the percentage of water-stable aggregates was determined. In the experiments reported here, no corrections have been made for the initial moisture contained in the air-dry samples. Since the amount of sand larger than 0.25 mm. in the four soils used is very small, no attempt was made to correct the weight of material retained by the sieves for the presence of primary particles.

#### EXPERIMENTAL RESULTS

For each of the four soils, triplicate determinations were made at oscillation periods of 1, 2, 4, 8, 16, 32, and 64 minutes following a 3-minute presoaking. To study the effect of the duration of the presoaking period, similar sets of determinations were made following 30- and 300-minute presoakings. A preliminary plot of the data indicated that the relation between aggregate stability and the length of the oscillation period was an exponential one and therefore could be shown advantageously if plotted on logarithmic coordinates. The data obtained are summarized in table 1. The weight of soil retained on the sieve is in each case the mean of the triplicate determinations, the individual values of which seldom varied more than 10 per cent from the mean value.

The analytical relations between the water-stability of the aggregates of the four soils and the intensity of the agitation as determined by the length of oscillation period were obtained by calculating the respective regression equations from the data given in table 1. The results of these calculations, which are shown in table 2, indicate that the aggregate stability of each of the soils can be characterized by two parameters; namely, the  $y$ -intercept and the slope of the regression equation. An analysis of variance of these parameters revealed that the differences between the mean intercept values for the four soils were highly significant. Similar results were obtained from an analysis of the mean slope values. The differences in intercept and slope values arising from variations in the length of the presoaking period were not statistically significant.

TABLE 1

*Weight of water-stable aggregates retained on a 0.25-mm. sieve after various lengths of oscillation and preliminary soaking*

A 5-gm. sample of aggregates of 4.7- to 2.0-mm. size class was used

OSCILLATION TIME		MUSCATINE		MARSHALL		CLINTON		KNOX	
(T)	log T	W	log W	W	log W	W	log W	W	log W
min.		gm.		gm.		gm.		gm.	
<i>5-Minute soaking</i>									
1	0.0	4.22	0.625	2.80	0.448	3.42	0.534	1.79	0.253
2	0.3	4.02	0.604	2.12	0.326	2.56	0.408	1.34	0.127
4	0.6	3.85	0.585	1.69	0.228	1.98	0.296	0.78	-0.106
8	0.9	3.59	0.555	1.54	0.187	1.59	0.201	0.45	-0.342
16	1.2	3.44	0.536	1.36	0.133	1.55	0.190	0.59	-0.232
32	1.5	3.02	0.480	1.27	0.104	0.84	-0.068	0.38	-0.416
64	1.8	2.59	0.413	0.90	-0.047	0.56	-0.252	0.26	-0.588
<i>30-Minute soaking</i>									
1	0.0	4.41	0.645	2.70	0.431	3.10	0.492	1.32	0.120
2	0.3	4.06	0.609	2.41	0.382	2.34	0.369	1.08	0.033
4	0.6	3.73	0.572	1.85	0.267	1.94	0.287	0.73	-0.136
8	0.9	3.52	0.547	1.91	0.281	1.48	0.170	0.56	-0.252
16	1.2	3.70	0.569	1.43	0.155	1.15	0.060	0.41	-0.388
32	1.5	3.30	0.518	1.53	0.184	0.85	-0.070	0.27	-0.560
64	1.8	2.51	0.399	0.95	-0.023	0.53	-0.274	0.21	-0.670
<i>300-Minute soaking</i>									
1	0.0	4.07	0.610	2.56	0.408	3.03	0.481	1.25	0.096
2	0.3	4.02	0.604	2.21	0.344	2.77	0.442	1.20	0.079
4	0.6	3.95	0.597	2.00	0.301	1.99	0.299	0.70	-0.152
8	0.9	3.95	0.597	1.96	0.292	1.31	0.117	0.41	-0.388
16	1.2	3.82	0.582	1.74	0.240	1.00	0.000	0.29	-0.538
32	1.5	2.96	0.471	1.04	0.017	0.91	-0.040	0.32	-0.493
64	1.8	2.71	0.433	0.89	-0.051	0.67	-0.174	0.26	-0.588

TABLE 2

*Regression equations showing the relation of weight of water-stable aggregates to length of oscillation period*

Calculated from data in table 1, the values of  $a$  and  $b$  in the equation  
 $\log W = a - b \log T$  are given

PRELIMINARY SOAKING PERIOD	MUSCATINE		MARSHALL		CLINTON		KNOX	
	$a$	$b$	$a$	$b$	$a$	$b$	$a$	$b$
<i>minutes</i>								
3	0.643	0.111	0.414	0.241	0.572	0.407	0.214	0.445
30	0.650	0.110	0.440	0.223	0.512	0.405	0.143	0.453
300	0.643	0.097	0.446	0.249	0.556	0.384	0.101	0.426
All preliminary soaking periods combined	0.645	0.106	0.433	0.238	0.547	0.399	0.153	0.441

Since the duration of the initial soaking had no significant effect on the resulting regression lines, the values for the 3-, 30-, and 300-minute presoaking

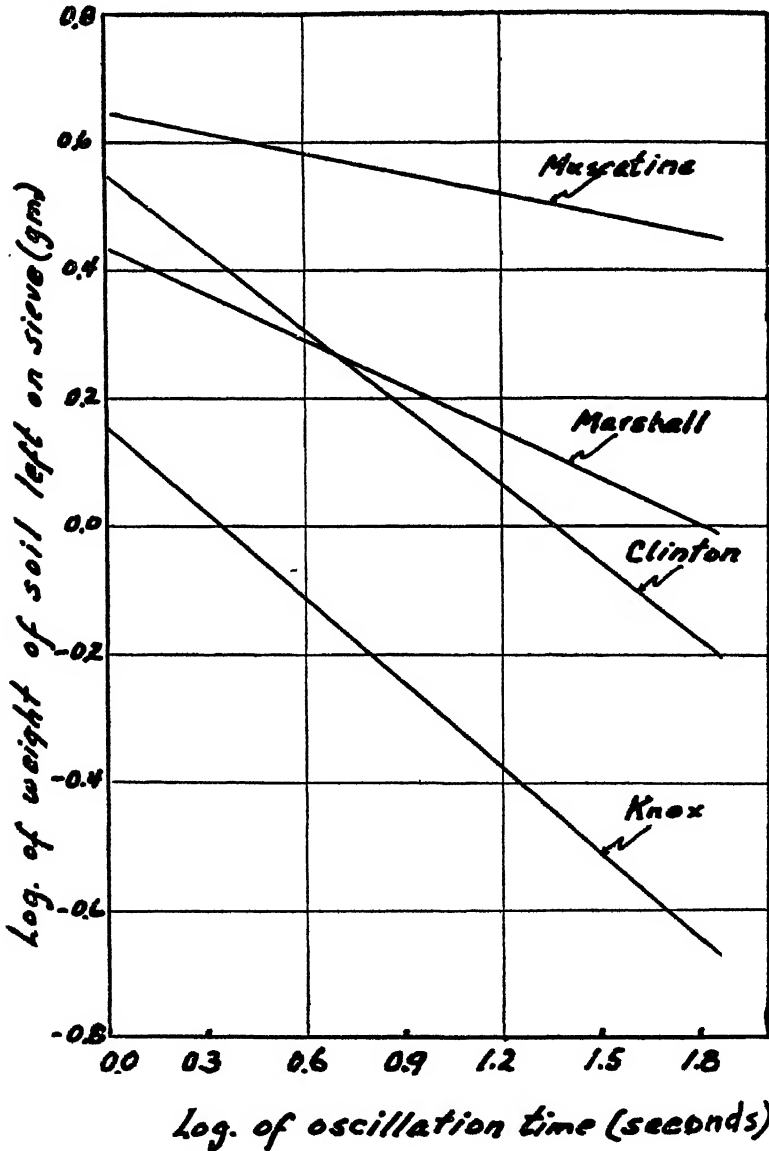


FIG. 1. REGRESSION LINES SHOWING RELATION BETWEEN AGGREGATE STABILITY AND INTENSITY OF AGITATION FOR FOUR IOWA SOILS

curves were combined for each soil to give the four curves shown in figure 1. These curves emphasize the need for more than a single value for the characterization of aggregate stability. For example, if the four soils were arranged in

order of decreasing stability as measured after a 1- or 2-minute period of oscillation, the order would be Muscatine, Clinton, Marshall, Knox. If, however, a similar ranking were made from measurements made following an oscillation period of 8 or more minutes, the order would be Muscatine, Marshall, Clinton, Knox. Since many investigations of soil structure involve relatively small differences in stability, it is quite possible that conclusions based on single-valued measures would frequently be altered if the procedures used in obtaining those measures were changed slightly.

From the foregoing data, it would appear that both the "initial stability" (the  $y$ -intercept) and the "rate of disintegration" (the slope of the regression line) should be used in characterizing the water stability of soil aggregates. In general, soils having high initial stabilities and low rates of disintegration will be preferred to those having either low initial stabilities or high rates of disintegration.

TABLE 3

*Size distribution of water-stable aggregates retained on the 0.25-mm. sieve expressed as relative values with the amount of the 0.50- to 0.25-mm. class arbitrarily taken as 1.0*

Average value for all oscillation periods

SOILS	SIZE CLASSES			
	> 1.0 mm.	1.0 to 0.5 mm.	0.5 to 0.25 mm.	0.25 to 0.10 mm.
Muscatine.....	11.2	4.1	1.0	0.51
Marshall.....	1.9	2.4	1.0	0.60
Clinton.....	1.4	2.6	1.0	0.80
Knox.....	2.5*	2.1	1.0	0.85

\* Composed largely of organic debris and primary mineral particles.

tion or both. Of the two parameters, the slope value should probably receive greater consideration in evaluating aggregate stability than the intercept value, although neither should be used as the sole criterion.

After the water-stable aggregates that had been retained by the 0.25-mm. sieve following the several periods of oscillation had been oven-dried and weighed, they were subjected to a period of dry-sieving. This sieving was performed by placing the sample on the upper of a nest of four 2-inch sieves having openings of 1, 0.5, 0.25, and 0.10 mm. The nest of sieves was shaken 20 times in a horizontal plane in as reproducible a manner as was manually possible. The weight of material retained on each sieve was determined and expressed in terms of the weight of material retained on the 0.25-mm. sieve. This method of tabulating the results was employed because it was desired to compare the size distribution of the water-stable aggregates of the four soils which, as shown above, have widely different absolute amounts of water-stable aggregates. A summary of the average relative weights of aggregates of the four soils is given in table 3.

It seems clear that the stable aggregates larger than 0.25 mm. in these four soils are distributed quite differently among the four size classes studied. The water-stable aggregates of the Muscatine soil contain a high proportion of

aggregates > 1.0 mm. and progressively smaller proportions of the three smaller sizes. In both the Marshall and Clinton soils the 1.0- to 0.5-mm. size class is larger than the other classes. The relatively high value of the >1.0-mm. fraction in the Knox soil is due to occasional  $\text{CaCO}_3$  concretions and many bits of undecomposed organic debris. Because of the extremely low absolute magnitude of the reference fraction (0.5 to 0.25 mm.) this resulted in abnormally high ratios for the largest size class. The material retained on the 1.0-mm. sieve was found to be invariably composed of debris and an occasional primary particle.

The size-fractionation studies of the water-stable aggregates indicates that, in addition to their difference in initial stabilities and rates of disintegration, the aggregates of the four soils possess quite different size distributions even though the material initially agitated was in each case of a single size class. On the basis of the samples studied in this investigation, it appears that high initial stability and low rate of disintegration may be associated with a high proportion of the larger classes of water-stable aggregates. As the rate of disintegration increases, there is a tendency for the mode of the size-distribution curve to shift to a smaller size class.

#### SUMMARY

A study of the water stability of aggregates sieved from four Iowa soils was made. The weight of water-stable aggregates ( $W$ ) retained on the 0.25-mm. sieve had the following functional relation to the length of the period of oscillation ( $T$ ):

$$\log W = a - b \log T$$

The two parameters  $a$  and  $b$  were designated as the "initial stability" and the "rate of disintegration" and were suggested as values to be used in characterizing aggregate stability. It was found that both of these parameters differed significantly among the four soils studied but that wide variations in the length of the preliminary soaking of the aggregates had no significant effect on either of them. Increases in the value of the rate of disintegration were associated with a shift of the size-distribution curve towards the smaller size classes.

# SEASONAL VARIATION IN LEAF AND SOIL POTASSIUM<sup>1</sup>

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The position occupied by leaf analysis as a diagnostic measure of the sufficiency of nutrient elements for normal plant growth was recently defined by Thomas (9). Literature on this subject has been increasing greatly because of the need for a reliable, rapid method of detecting deficiencies, or excesses, before damage to the plant occurs. Frequently a soil analysis or a total analysis of the mineral composition of a plant assumes the post-mortem rather than the diagnostic role. Furthermore, in cases of the minor or trace elements, the range between deficiency and toxicity is often so narrow that accurate measurement of important differences in the soil alone is inconclusive. This latter fact has stimulated analysis of the plants growing on the soil, since they could serve in an accumulative capacity. Such a sponge-like role presupposes that all of a nutritive element available to the plant roots would be absorbed if conditions allowed. Leaves, stems, and roots have been analyzed. Crops with a preponderance of stem tissue or root tissue soon were recognized as special cases, and interpretation of data obtained from their analysis was thus complicated. Hoffer (6) and other (5, 8) have used tissue tests, and still others have substituted plant parts for the whole plant. Recognition of the leaf as a somewhat sensitive indicator of nutrition status has focused interest here. Many investigators have used whole leaves (9); some have removed the petioles before analysis (7, 10); others have used old leaves, the growing tips, or the skeleton of the leaves after a special treatment to remove parts of the tissue (1, 2, 3); and some have used specific leaves, such as the first mature leaf behind the growing tip (4, 10). Thus a search was made to locate a particular leaf of a specific crop that would best represent or indicate by a chemical analysis its mineral requirements for normal growth. Discovery of such a sensitive leaf would eliminate the necessity of destroying the plant in diagnosis and aid in applying the cure before damage is done.

The results of this search have not been entirely satisfactory to date; much progress has been made, yet many problems have arisen (9). These problems include, among others, the recognition of normal growth, the effects of varietal differences, climate, soil type, differences in level of available nutrients, and time of year or stage of growth.

The purpose of this paper is to present results obtained during a study of the leaf composition of cane fruits. This study is a continuation of experiments

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previously reported (4) and is concerned chiefly with the variations in leaf composition throughout a growing season, with emphasis on the role of potassium. Where black and red raspberries are concerned, soil samples were taken concurrently with leaf samples to study the correlation between supply of available potash in the soil and leaf composition.

#### MATERIALS AND METHODS

This investigation was carried out with established major and minor element fertilizer trials on three distinctly different soil types. They are Powell silt loam (heavy subsoil phase), a soil type near Gresham, Oregon, which has responded slightly to potash fertilization of red raspberries; Olympic silty clay loam, an eroded hill soil from Lacombe, Oregon, growing black raspberries and responding most consistently to potash applications used in this study; Powell silt loam from Troutdale, Oregon, supporting Boysenberries, considered one of the better soils of the Powell series and responding erratically to K applications; and Amity silty clay loam from Woodburn, Oregon, a soil which has given some positive response to K fertilization of gooseberries.

The leaf selected for analysis was the first mature leaf behind the growing tip (4), some 50 to 100 leaves being composited from each row. Travel restrictions limited sampling to each 6 weeks, and in some cases not all crops were sampled at the same growth period. Surface (0-6 inches) and subsurface (6-12 inches) soil samples were taken from each plot when leaves were collected from the red and black raspberry plots. These samples were composited from three or more borings collected with a 3-inch post-hole digger and smaller auger.

Exchangeable potassium in the soil was extracted with neutral normal ammonium acetate, precipitated as cobaltinitrite and estimated with ceric ammonium hexanitrate and sodium oxalate titration. Leaf samples were oxidized with a mixture of nitric and perchloric acids (11).

#### RESULTS AND DISCUSSION

##### *Leaves*

The ultimate value of leaf analysis as a guide to potash fertilization of cane fruits for maximum yield in Oregon is not known. Interpretation of the results of this study, however, indicates some possibilities. In table 1 are summarized data obtained during a complete growing season from analyses of red raspberry, black raspberry, Boysenberry, and gooseberry leaves. Sampling intervals were timed to correspond roughly to the early spring leaves produced before much growth was made (preblossom), leaves taken when the plants were in full bloom (blossom), leaves taken when the plants were at the height of fruit production (fruiting), and those leaves that remained after harvest was completed and new fall growth evident (postharvest). In the case of the gooseberries, leaves sampled in the fall were those produced after the plant had recovered from de-

foliation<sup>3</sup> suffered during harvest and came from the old wood rather than from new growth.

TABLE 1

*Potassium composition of cane fruit leaves as affected by K fertilization and stage of growth*

FIELD TREATMENT		PREBLOSSOM K	BLOSSOM K	FRUITING K	POST HARVEST K	FALL GROWTH K	YIELD 4-YEAR AV.
pounds		per cent	per cent	per cent	per cent	per cent	tons
<i>Red raspberries—Powell silt loam</i>							
None		1.19	1.83	0.47	1.07	....	2.60
500	5-20-0	1.46	1.28	0.80	0.67	....	2.25
500	5-20-10	1.93	2.19	1.00	0.84	....	2.76
1000	5-20-10	1.49	1.60	1.17	0.90	..	2.37
1500	5-20-10	1.55	2.00	1.47	0.90	....	2.40
<i>Black raspberries—Olympic silty clay loam</i>							
None		0.96	0.09	0.16	0.43	....	0.52
500	5-20-0	0.90	0.10	0.21	0.25	....	0.43
500	5-20-10	1.21	1.26	1.01	0.35	....	0.58
500	5-20-15	1.38	0.81	0.19	0.55	....	0.88
500	5-20-20	1.63	0.72	0.57	0.38	....	1.18
<i>Boysenberries—Powell silt loam</i>							
None		....*	1.83	1.53	(3.96†)	....	4.48
500	5-20-0	....	0.90	1.37	0.90	....	4.37
500	5-20-10	....	1.60	1.47	1.27	....	4.44
1000	5-20-10	....	1.67	1.97	0.87	....	4.61
1500	5-20-10	....	2.07	1.47	1.60	....	4.52
None		1.07	2.27	1.33	1.02	....	4.04
500	5-20-0	1.47	1.47	1.37	1.42	....	3.98
500	5-20-10	1.70	2.43	0.97	1.33	....	4.36
500	5-20-15	1.50	2.43	2.17	1.07	....	3.94
500	5-20-20	2.07	2.43	0.73	0.97	....	3.89
<i>Gooseberries—Amity silty clay loam</i>							
None		....	0.93	0.19	0.77	0.30	1.52
500	5-20-0	....	0.87	0.09	0.86	0.70	1.83
500	5-20-10	....	1.30	0.38	1.27	1.07	1.66
500	5-20-15	..	0.93	0.27	0.73	0.77	1.75
500	5-20-20	..	1.07	0.91	1.07	1.50	1.42

\* Not sampled.

† New growth, not comparable.

Red raspberry plants growing on Powell silt loam received increasing increments of a 5-20-10 fertilizer applied first in the early spring of 1939 by the

<sup>3</sup> Hand harvest of gooseberries results in partial defoliation.

Station soils department. In table 1 the unfertilized and the 5-20-0 plots are included for comparison. The preblossom stage represents, more or less, the starting point of the growing season, and at this time fertilized and nonfertilized plants were similar in composition. Weathering agencies through the previous winter had released nonavailable potassium (12), which, with that stored in the plant body, was sufficient to give all plants an equal start. As the season progressed to the blossom and fruiting stages, however, differences were magnified by increasing needs of the maturing berries. Only those plots receiving potash fertilizers were able to maintain leaf potassium of 1.00 per cent or more while berry production was under way. Application of nitrogen and phosphate produced more vigorous and larger foliage with a subsequent heavier drain on stores of available potash. Because the Powell soil was not particularly deficient in potash, supplies were sufficient to enable the plants to maintain fairly high leaf potassium. Where no potassium was added, the plants were smaller and less vigorous and contained only 0.47 per cent K during berry production as compared with 1.47 where the heaviest fertilizer application was made. As the peak requirement was passed with the completion of berry harvest, potassium was shifted into new cane growth and, consequently, concentration of K in the old leaves decreased. It is of interest to note that untreated plants had the highest K composition during this period. Since this plot produced less fall growth, it is likely that potash already in the leaves was not transported to such extensive growing areas as in the treated plots.

The yields obtained are expressed as the 4-year average; the lowest was from the N-P plot, and the highest was from the plot receiving 500 pounds of 5-20-10 fertilizer. The low yield from the N-P plot was likely due to increased vigor and growth from added nitrogen and phosphorus while potash was thus made somewhat limiting. This is further supported by the fact that the untreated plot outyielded all but one K-treated plot (500 pounds of 5-20-10).

Black raspberries grown on Olympic silty clay loam were fertilized with materials of increasing ratio of potash to phosphate and nitrogen rather than with increasing rates of a constant ratio material (table 1). Apparently the low nutritional status of the unfertilized soil was balanced, because when the general fertility was improved by application of nitrate and phosphate, potash importance, as measured by berry yields, was approximately trebled.

At the beginning of the growing season, plants in the unfertilized plot were small, light green, and presented a general unhealthy appearance. The leaves were small and contained nearly 1.00 per cent K, which, if maintained, is perhaps enough to support a good yield. But this level was not maintained. It dropped to one-tenth of this value during the blossom stage, increased slightly during fruit production, and by the end of the season had reached about 50 per cent of the original value. Increase in K content of leaves sampled was closely related to translocation of potassium from senescent tissues such as dying canes and leaves which were more plentiful on this untreated than on any treated plot. As the K reserves were drawn upon by blossom and fruit production, the older leaves began to show evidence of potash starvation. The leaf edges and tips turned brown,

curled somewhat, and finally turned black; a condition known as leaf "scorch" developed. This condition in modified form has been found with red raspberries, Boysenberries, and also gooseberries. This symptom of K starvation has been shown to be due to the extremely low potash content of the leaves (4). In all cases, potash applications alleviated this condition, and in some cases it was eliminated. Leaf "scorch" has also been found to be closely related to excessive manganese absorption.<sup>4</sup> Leaves exhibiting bronzing or scorching contain unusual quantities of manganese. This fact is being studied further.

In the preblossom stage of growth, leaves were found to contain approximately 1.00 per cent K, the untreated being slightly lower and the most heavily treated somewhat higher than this value. In the blossom stage differences were most apparent, ranging from 0.09 in the check to 1.26 per cent in leaves from the 5-20-10 plot. Despite heavier applications, the other potash-treated plots had leaves that contained less than 1.26 per cent K probably because of greater total absorption as measured by leaf, cane, and berry growth. The berry yields were high enough to account partly for a lower leaf K in these two plots. The lower leaf K was accompanied by slight bronzing and scorching. Regardless of greater potash removed in the fruit from treated plots, leaves from all plots were similar in potash composition at the end of the season. The larger, more vigorous plants on the K-treated plots probably were in better condition, however, to resist winter injury. This is important in giving the plants a better chance for new cane growth in the fall in addition to a slightly higher potash level to start from in the spring. Thus, K fertilization of blackcaps on Olympic soil not only produced more berries the current year but alleviated scorch and allowed accumulation of greater quantities of available or soluble K for next year's crop.

Boysenberries were grown on a better grade Powell, except for the K-variation plots, than that on which red raspberries were produced. The plots included tests of rate of application and increasing ratios of K to N-P. This soil was not deficient in potash, and only slight increases in yields were obtained with N-P-K fertilization regardless of treatment.

Leaf composition varied with the stage of growth, and was in most cases above 1.00 per cent K. Since damaging leaf scorch was not found on these plots and since it was found in plots where the K content of the leaf fell below 1.00 per cent, this quantity may be considered as a more or less critical level. This confirms the findings of Clark and Powers (4). With the Boysenberry K-ratio trials the leaf potassium content, determined at 6-week intervals, varied from less than 1.00 per cent to more than 2.4 per cent, depending on the potash treatment and the stage of growth. The highest leaf potash was not found on the potash-treated plots, but in general these plots did have plants whose leaves maintained a relatively high level of total potassium. It is not known what soil differences in available potassium existed in these plots, although nearby virgin soils were well supplied with available potash.

<sup>4</sup> Unpublished data.

In the preblossom stage the leaf potassium content of the check plot was 1.07 per cent and that of the high-potash plot was 2.07 per cent. These values reached a maximum of 2.27 and 2.43 per cent respectively during the blossom stage and then fell off during the fruiting stage. The data indicate a rapid decrease in the concentration of potassium in the leaves of the high-potash plot, likely due to berry production and also to the production of a more luxuriant, bushy growth of the canes. Regardless of treatment, the potassium content of leaves appeared to concentrate around 1.5 per cent in the preblossom and 2.4 per cent in the blossom stage. In the fruiting period, erratic values were found, varying from 0.7 to 2.2 per cent. At the postharvest period, however, all treatments had leaves that contained about 1.0 per cent potassium. No correlation was apparent between potassium content of leaves and yield.

The potassium content of leaves from the rate trials varied slightly with treatment and widely with time of sampling. In general the levels were similar to those found in the potash-ratio trials.

With gooseberries there was little correlation between potassium content of leaves and potassium applications, probably because the gooseberry bush is fed by roots which penetrate to soil depths not immediately affected by potash fertilizers. Highest yield increase due to potassium additions was obtained from the medium-potash plot. Potassium found in leaves from this plot was 0.93, 0.27, 0.73, and 0.77 per cent respectively in the four periods sampled, 0.27 being the level found during fruit production. Additional potash increased the leaf content, but this was not reflected in the yield; actually the lowest yield obtained was that from the high-potash plot, indicating that potash applications to this plot upset the nutrient balance and encouraged luxury consumption.

Plots receiving potash fertilizers were able to deliver more potash to the berries throughout the growing season and to maintain a higher potassium level to supply nutrient for the following year's new growth. This was probably the chief benefit derived from applications heavier than the medium rate. Increasing the potassium content of a leaf by fertilizer applications likely does not benefit the leaf or the plant unless the element is at a critical level and the plant is in a critical growth period, such as that during fruit production.

Bronzing of gooseberry leaves is definitely related to the potassium content. Low values for potassium content are usually found where bronzing has occurred, and the degree of bronzing is increased as the potassium decreases. From one third to one half as much potassium is found in bronze leaves as in normal green leaves, even though the leaves are removed from potash-fertilized plants.

Establishment of a critical level for leaf potash must be done at the time when needs are greater than the supply. With cane fruits this probably is near the blossom period. The purpose of diagnosis is to enable application of a cure before malnutrition proves fatal; diagnosing K deficiencies in the blossom stage of cane fruits, or later, approaches a post-mortem diagnosis. The damage has been done before treatment begins, and chemical analysis of leaves during the blossom stage, though facilitating a prediction of what may happen, cannot indicate the treatment to prevent undesirable results. Analysis of leaves in the pre-

blossom stage will reflect the effects of the previous year's treatment but will not necessarily indicate the K-supplying power of the soil or what will happen when fruit production demands for K are made. The value of later leaf samplings becomes less and less as maturity is passed, especially for the current year's crop.

To be most valuable in diagnosing needs and prognosticating treatments of cane fruits, leaf analysis, therefore, may best be based upon an early stage of growth and a leaf more sensitive to K fluctuations than is the first mature leaf behind the growing tip. It is possible that the oldest leaf, from which translocations occur as demands are increased, would be more sensitive. Not only would this leaf allow an earlier diagnosis, as pointed out by Thomas (9), but it also would assist prognosis and treatment of the current year's crop. These older leaves, however, may be more subject to disease.

### *Soils and leaves*

It has long been recognized that potassium is subject to luxury consumption. In order to study correlation of supply and demand for this element, soil samples were taken concurrently with leaf samples from the Powell and Olympic surface soils. Table 2 shows the quantities of exchangeable potash present in the first two 6-inch layers of soil at four intervals during the growing season.

The Powell soil used was not low in exchangeable potassium, and small yield increases due to K applications would be expected. The untreated surface soil contained 173 p.p.m. of exchangeable K, which, if maintained, would be sufficient. The surface layers of the K-treated plots contained 385 to 580 p.p.m. in the preblossom stage. The subsurface layer varied from 96 p.p.m. in the untreated to 366 in the most heavily treated plot. Concurrently sampled leaves (see table 1) were found to contain potassium in amounts somewhat paralleling the exchangeable supply.

When heavier demands were made on the exchangeable supply during the blossom period, changes in exchangeable K were most marked in the 6-12-inch layer. Absorption had depleted the supply to or below a level critical for good growth in the plots receiving no K fertilization. Exchangeable K in the check plot reached a low of 9 p.p.m., which was but 10 per cent of the initial figure. The corresponding amount in the plot treated with 1000 pounds 5-20-10 was 93 p.p.m., or 22 per cent. Since the blossom stage is critical in the life of the plant so far as fruit production is concerned, maintaining a level of exchangeable K sufficiently high to prevent depression of growth and to facilitate berry formation at this time is of utmost importance.

It is known that the available moisture throughout the blossom period may be limiting, and unless it is controlled by irrigation practices, some drying and baking in the immediate surface occurs. This forces the root system to absorb from lower layers, hence removal of exchangeable K in the second soil layer approaches completion while in the surface it is relatively unchanged. Two possibilities of alleviating this condition are, first, proper irrigation and, second, fertilizer placement. If K applications were made to the area where the roots are effecting major absorption, the exchangeable level could be kept high enough

to prevent growth limitations imposed by a deficient supply of potash. The present practice is to apply fertilizers to the surface or in a shallow furrow and then let moisture and tillage practices get them into the areas where roots are established. So far as potassium is concerned, irrigation or natural rainfall would be quite inefficient, except over a period of time, since depth penetration of added potassium probably is not great.<sup>5</sup> Furrow applications are complicated by the root habit of such plants. Broadcast fertilization is wasteful with this type of crop because of the relatively unused area. Fertilizing in a furrow about 6 inches deep along each side of the irrigated berry row would be ideal. Results of furrow and broadcast applications to Boysenberries are available, and

TABLE 2  
*Seasonal levels of exchangeable K in soil as modified by potash applications*

FIELD TREATMENT		PREBLOSSOM STAGE, EXCHANGE K		BLOSSOM STAGE, EXCHANGE K		FRUITING STAGE, EXCHANGE K		POSTHARVEST STAGE, EXCHANGE K	
		0-6 inches	6-12 inches	0-6 inches	6-12 inches	0-6 inches	6-12 inches	0-6 inches	6-12 inches
pounds		p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
<i>Powell silt loam</i>									
None		173	96	238	9	148	39	207	112
500	5-20-0	236	135	162	36	130	71	117	129
500	5-20-10	385	136	255	82	220	140	405	267
1000	5-20-10	521	211	501	93	535	282	512	155
1500	5-20-10	580	366	475	127	740	495	560	318
<i>Olympic silty clay loam</i>									
None		107	59	156	30	140	29	118	66
500	5-20-0	198	148	102	21	78	22	67	22
500	5-20-10	134	78	68	60	146	50	126	99
500	5-20-15	252	33	316	53	152	47	182	66
500	5-20-20	292	174	109	30	151	67	179	195

although the furrows were only 3 to 5 inches deep, a 5-year average increase of 0.26 ton for furrow application was obtained.

As the season progressed, fluctuations in exchangeable soil K were noted (table 2). These were the result of absorption by the crop and upward leaching due to evaporation. At the end of the season the exchangeable K levels of all plots appeared to approach closely the level at the beginning of the season. The release of insoluble forms of potassium, studied by Wood and DeTurk (12) and others, in equilibrium reactions, in addition to falling leaves, upward leaching, translocation out of the plant roots, and weathering agencies accounts for this return to the original status. Re-establishment of the original status was most rapid where potash applications had been made, the N-P plot being the slowest to return. Maximum K depletion of the soil occurred in the first 6 weeks, followed by a return to near the original status as the season ended. Surface

<sup>5</sup> Unpublished manuscript.

soil of the N-P plot had not recovered by the end of the growing season, although the subsurface appeared to have done so. With the treated plots, both surface and subsurface had recovered because of the greater K-supplying power.

It is noteworthy that the Olympic soil contained significantly less exchangeable K in the surface horizons that did the Powell soil. This explains the more consistent yield increases to potash fertilization obtained from the Olympic soil. In general, behavior of the N-P plot of both soil types was similar; that is, a depletion occurred mainly in the first 6 weeks, the subsurface layer tended to return to initial status more rapidly than the surface, and leaf composition continued to decrease from the original level as the season advanced. Leaves from the N-P plot never contained as much as 1.00 per cent K, bronzing or "scorch" was increasingly prevalent throughout the season, and the plants were small.

The treated and untreated Olympic soils responded similarly, but because of added potassium the supplying power of the treated soil was greater and the return to near equilibrium status was more rapid. Exchangeable potash in the surface was generally reduced before the plants blossomed but gradually increased, while that in the subsurface was reduced below critical concentrations but rose until the end of the growing season, when the original exchangeable level had been restored.

#### SUMMARY AND CONCLUSIONS

A study of seasonal variation in potash content of selected leaves from red raspberry, black raspberry, Boysenberry, and gooseberry plants, together with changes in exchangeable potassium content of two soils, is reported. Four soils, Olympic silty clay loam, Powell silt loam (a deep and a shallow phase), and Amity silty clay loam, were studied. Fertilizer applications to the soils in the field ranged from 0 to 1,500 pounds per acre of 5-20-10 and included, in some cases, increases in rates of application and, in others, increases in ratio of K to the N-P applied. Check plots and N-P plots were included for comparison.

It was found that the K content of the first mature leaf behind the growing tip was greatly influenced by K fertilization and stage of growth. At the beginning of the season's growth the carry-over of the previous year's fertilization was closely related to the amount of K applied. Passing through growth stages of preblossom, blossom, fruiting, and postharvest, leaves showed wide variations in K content. With the exception of black raspberries, the potash content was highest in the blossom stage. In red and with black raspberries, the lowest leaf potash was found in the postharvest period. In Boysenberries, leaf composition varied widely with treatment and stage of growth. Gooseberry leaves contained minimum potassium during the fruiting stage.

Relationship of exchangeable K in the soil to leaf composition was found to be erratic. This indicates that either there is no correlation between these quantities or that a more sensitive leaf than the one sampled exists. The latter case seems most likely. There was little relationship between leaf composition and yield in this study. Yield data, however, showed that application of N-P fertilizers increased the need for K except with gooseberries. Bronzing or leaf scorch was found wherever leaf K was much lower than 1.00 per cent prior to the fruiting



stage. Any attempt to set a level of leaf K below which it would prove advantageous from a yield standpoint to make K applications must be based on the stage of growth. Also, critical levels of leaf potassium below which K deficiency will appear, either as visible symptoms or as decreased yield, must be correlated to stage of growth. Potash is needed in larger quantities during the blossom stage, in which fruit production actually begins, than in any other stage. Establishing a need for potash at this stage is too late, however, to help the current year's crop materially. Use of a more sensitive leaf or a leaf that can be sampled earlier in the season, such as the most mature or senescent leaves, is suggested. Recent evidence obtained suggests that the use of a leaf adjacent to the fruiting tip will correlate leaf composition and need for potash with ultimate yields. This possibility is being investigated further.

Potash absorption from the 6- to 12-inch soil layer was found to be particularly high during the blossom stage of growth of both red and black raspberries, although wide variations in exchangeable K content of the surface soil were found. This fact, together with yield increases obtained from fertilizer trials initiated in 1939 by the soils department, suggests that greater emphasis should be given to fertilizer placement, especially where there may be a nutrient deficiency and roots are restricted to a limited area, as with the Olympic soil. Instead of applying potash to the surface of such a soil, a furrow at least 4 to 6 inches deep should be made so the fertilizer can be placed nearer the roots. Yield increases obtained from applications made in a shallow (3 to 5 inches) furrow, where potash is not particularly limiting, emphasize this.

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# THE MINERALOGICAL APPROACH TO SOME SOIL PROBLEMS<sup>1</sup>

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The soil mineralogist is interested in evaluating the soil in terms of its mineral content and in utilizing the information obtained along with that of the chemist, the biologist, and the physicist in dealing with problems of soil classification, formation, and fertilization. In other words, soil mineralogy is that branch of soil science which deals with the nature of the inorganic part of the soil, the framework upon which, in most cases, all other soil characteristics develop.

The mineral groups of interest from a soil standpoint are relatively few in number. Minerals are classified generally as primary or secondary: primary minerals are those that are formed by the solidification and crystallization of a molten magma under varying conditions; and secondary minerals, those formed as decomposition products of primary minerals. The crust of the earth is essentially igneous. Clark estimates 95 per cent igneous (including metamorphic), 4 per cent shale, 0.75 per cent sandstone, and 0.25 per cent limestone as the average distribution of various rock types to a depth of 10 miles. In addition to his estimate of this rock distribution, he (1) has further estimated the average mineral composition of the lithosphere as 57.8 per cent feldspar, 12.8 per cent quartz, 16 per cent amphiboles, 3.6 per cent mica, 8.0 per cent accessory minerals, 1.1 per cent clay, 0.5 per cent carbonates, and 0.2 per cent limonite. The surface of the earth, in which soil investigators are generally interested, is, however, underlain by 75 per cent sedimentary rocks and only 25 per cent igneous rocks. In most cases, therefore, soils have been derived generally from pre-existing sediments and are a part of a cycle of weathering which started with igneous rocks and the minerals of which they are made.

The average mineral composition of sedimentary rocks as calculated by Krynine<sup>3</sup> gives a very different picture of the distribution of mineral groups involved in the formation of soils. His estimate places quartz as the most abundant mineral, micas and carbonates in about equal proportions, followed by clays, feldspars, accessory minerals, and limonite in the order named.

These estimates are set forth in table 1, which shows that the important mineral groups with which soil investigators are concerned are only about eight in number.

Most minerals occur as members of a series, and these series are established on the basis of chemical and physical similarities. The chemical and physical

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<sup>3</sup> Personal communication.

properties of minerals within a series are therefore variables, and any studies involving the characteristics of a mineral must necessarily commence with the determination of the series and then the position of the mineral in the series. The members of a series which exhibit the limiting properties of that series, then, are termed "end members," and for most series the end members are known.

TABLE 1  
*Mineral composition of the crust and the average sediment of the earth*

MINERAL	CRUST*	AVERAGE SEDIMENT†	AVERAGE SEDIMENT, CARBONATE-FREE
	per cent	per cent	per cent
Feldspar.....	57.8	7.0	8.7
Quartz.....	12.8	38.0	47.5
Amphibole.....	16.0	...	....
Mica.....	3.6	20.0	25.0
Accessory.....	8.0	3.0	3.8
Clay.....	1.1	9.0	11.2
Carbonates.....	0.5	20.0	....
Limonite.....	0.2	3.0	3.8

\* Clark (1).

† Krynine, personal communication.

TABLE 2  
*End members, chemical compositions, and intermediate refractive indexes of some typical mineral series*

SERIES	END MEMBERS	CHEMICAL COMPOSITION	INTERMEDIATE REFRACTIVE INDEX
Plagioclase feldspar	Albite	$\text{NaAlSi}_3\text{O}_8$	1.529
	Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	1.583
Alkali feldspar	Orthoclase	$\text{KAlSi}_3\text{O}_8$	1.523
	Celsian	$\text{BaAl}_2\text{Si}_2\text{O}_8$	1.593
Muscovite	Muscovite	$\text{H}_4\text{K}_2(\text{AlFe})_6\text{Si}_6\text{O}_{24}$	1.582
	Phengite	$\text{H}_4\text{K}_2(\text{MgFe})\text{Al}_4\text{Si}_7\text{O}_{24}$	1.610
Biotite	Phlogopite	$\text{H}_4\text{K}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{24}$	1.564
	Annite	$\text{H}_4\text{K}_2\text{Fe}_6\text{Al}_2\text{Si}_6\text{O}_{24}$	1.690

The limits of the chemical compositions of some important mineral groups encountered in soil studies are set forth in table 2. It will be noted that in this list the minerals are tabulated by groups, and the compositions are those of the end members of the group as well as they are understood. Correlated with chemical composition are the optical properties of the members of these various series. Consequently, the determination of the optical properties of a mineral in a series establishes its chemical composition. Investigations of the characteristics of the minerals of soils, therefore, include the separation and subsequent study of these various mineral groups by chemical, optical, or x-ray procedures.

The fragmental materials of soils are generally coated or cemented together to

form aggregates by free iron oxides of varying degrees of hydration, and in some cases also by organic matter. The removal of these free iron oxides and organic matter is imperative to quantitative separation and identification of soil minerals. Organic matter can be readily destroyed by successive treatments with 10 per cent hydrogen peroxide; the removal of the free iron oxides is more difficult. In 1936 Truog and his associates (6) introduced nascent  $H_2S$  and oxalic acid to reduce and dissolve free iron oxides occurring in soils, and in 1941 the writer (2) utilized nascent hydrogen produced by the action of oxalic acid on aluminum in a soil suspension to reduce and dissolve free iron oxides prior to mechanical analysis and petrographic study. The soil separates obtained by either method consist of clean discrete mineral particles that can be separated successfully by means of heavy liquids and subsequently studied by appropriate methods to establish their identity and distribution.

In the study of the mineral characteristics of soils it has been found by various investigators that the mineral composition of the very fine sand (0.10–0.05 mm.), silt (0.05–0.002 mm.), and clay separates sets forth their most important mineral properties. This necessitates the mechanical separation of the iron-oxide-free soil into various sized particles. The various procedures for mechanical analysis of soils have been reviewed by Krumbein and Pettijohn (3, pp. 91–182). The removal of organic matter, and of free iron oxides, and the mechanical analysis are, therefore, necessary preliminary steps in establishing the mineral character of soils.

The next step is the separation of the mineral components of the very fine sand and silt into the various mineral groups for further study and identification.

The fact that the specific gravity of minerals is a fairly definite characteristic has proved very useful in effecting a separation of minerals, whereby their abundance can be estimated and identification greatly facilitated. Organic heavy liquids are generally utilized for these separations; mixtures of symmetrical tetrabromethane and nitrobenzene used according to Volk (7) have proved extremely useful in this procedure. For convenience it has been found that three specific gravity groups are generally sufficient to provide material for optical studies. These three groups are the "heavy group," minerals having a specific gravity greater than 2.90; the quartz group; and the feldspar group. In some cases where special attention is being given to certain specific minerals, separations based on narrower ranges may be made; however, in most cases these three specific gravity groups provide ample material for study.

Milner (5, pp. 607–612) lists some 650 different minerals according to their specific gravities, and from these data we find that about 83 per cent of the known minerals have specific gravities of 2.90 or greater, 12 per cent have specific gravities approximating quartz, and 5 per cent approximating microcline.

It is, therefore, to be expected that by far the greatest variety of minerals will be found in the specific gravity group of 2.90 or greater. This is true in most cases. The minerals of this group are generally listed as accessory, because even though there are a great variety their relative abundance as a group is small. As a mineral group, however, they are important because it is by study of them that

the mode of origin and identification of soils may be investigated. Marshall (4) utilized heavy mineral ratios in such studies with much success.

Another important property of the heavy mineral group which has received some attention but which has not been explored fully in varying content of the so-called minor elements in many of the minerals. This may have an important bearing on further work along those lines. Table 3 sets forth a list of common

TABLE 3  
*Heavy minerals common in soils and trace-element occurrences possible*

MINERAL	TRACE ELEMENT	MINERAL	TRACE ELEMENT
Zircon.....	Hf	Cyanite.....	
Tourmaline.....	B, Li	Hypersthene.....	
Chlorite.....		Enstatite.....	
Biotite.....	Cr, Li, Mn	Sillimanite.....	
Muscovite.....		Apatite.....	Fl, Mn, Sr
Epidote.....	Pb, Sr	Barite.....	Sr, Pb
Anatase.....	Cb, Ta	Fluorite.....	Yt, Ce, Di, La
Hornblende.....	Co, Fl	Hematite.....	
Augite.....		Leucoxene.....	
Garnet.....	Cr		

TABLE 4  
*Variation in feldspar content of very fine sand separates of different horizons of some soils of different origin*

FELDSPAR CONTENT OF SEPARATES FROM VARIOUS HORIZONS

	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>	B <sub>4</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Leetonia*.....	....	3.4	2.8	4.7	3.3	....	....	8.9	7.3	....
Gilpin*.....	2.4	1.5	1.0	0.5	....	....	....	tr.	tr.	tr.
Calvin*.....	7.4	3.6	1.8	1.1	1.0	....	....	0.9	1.3	....
Hagerstown, Pa.†.....	23.5	23.6	22.8	15.3	43.8	37.6	46.0	42.6	32.7	....
Hagerstown, Ind.†.....	21.6	21.8	....	22.4	17.2	....	....	19.7	....	....
Hagerstown, Va.†.....	18.5	....	....	9.6	....	....	....	6.6	10.0	....
Dunkirk, Va.†.....	12.1	19.4	16.4	11.5	....	....	....	10.9	....	....

\* Parent material sandstones and shales.

† Parent material limestone and dolomites.

heavy minerals that have been identified in soils by various investigators and shows the variety of minerals that may be encountered in work of this type, as well as certain trace elements that have been identified in several of them.

By far the most important mineral group found in the sand and silt fractions of soils is the feldspar. The abundance and variety of feldspars of the alkali and plagioclase series found in soils vary greatly. Some soils contain mere traces; others, relatively large quantities. The feldspars are important because they are the source of large amounts of potassium, calcium, and sodium, as well as

many of the clay minerals which occur in soils. Data are seriously lacking on the general distribution of feldspars in soils and the relation of feldspars to type of clay mineral formed under different environments. General statements are available, but specific data covering large areas of soils are lacking. In the study of potassium problems, information of this type would appear very helpful in the interpretation of results.

Table 4 sets forth the variation in feldspar content of some typical Pennsylvania soil profiles. Though the type of clay present has not been studied fully, preliminary work has shown a great variability between different soils, which is further reflected in the ability of these soils to fix and release potassium. The study of the role of feldspars in soils is a very fertile field for investigations not only of potash, but also of weathering processes and of soil formation. The first step, however, is a full understanding of the general distribution in soils of these very important mineral series.

Another important group of minerals, which are as widely distributed as the feldspars, are those of the muscovite series. Like the feldspars, they contain high amounts of potassium and, upon weathering, produce clay complexes quite different from those derived from the feldspars. Less is known about the general distribution and properties of muscovite in soils than of feldspars. Muscovite may be both primary and secondary. The distinction is difficult to make, particularly in attempting to study weathering processes in which muscovite is involved.

With information on hand concerning the mineral composition of the sand, silt, and clay separates, their composition and properties are the next phase of interest in designating the mineral character of a soil. The types of clay minerals present in the clay fraction may be ascertained by a variety of procedures, including x-ray, thermal, and chemical methods.

The influence of the mineral composition of the coarser fractions of soils upon the type of clay mineral produced by weathering reactions is not well understood. That differences should exist is obvious, but it must not be concluded that all of the clay fraction found in soils has been derived from the weathering of the sand and silt fractions. In many cases depositional processes can account for the presence of certain types of clay minerals in soils, and care must be exercised in the interpretation of results obtained.

#### SUMMARY AND CONCLUSIONS

A phase of soil science which has to do with the determination of the gross mineral composition of soils has been discussed. The mineral groups encountered in such studies are few, consisting of the feldspar, quartz, mica, heavy minerals, carbonates, and clay series. The variations in the abundance and distribution of these mineral groups in soils have much to do with their characteristics, mode of formation, weathering reactions under various climatic conditions, and agricultural utilization. It has been pointed out that certain of the minor elements may be found in the heavy mineral group, and also that the character and distribution of the feldspar and mica series may have a decided bearing on

the nature and type of clay fraction developed under different weathering conditions. It was emphasized that methods and procedures are now available for studies along the lines indicated, but that in many cases data still are lacking. This field of soil science deserves further consideration; all the details outlined should be taken into account so that a soil may be accurately characterized. When such information is available, it should be possible to eliminate some of the confusion in soil classification and in the interpretation of fertilizer experiments.

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# DISTRIBUTION OF TOTAL AND ALKALI-SOLUBLE ORGANIC MATTER BETWEEN THE WHOLE SOIL AND SOIL AGGREGATES OF DUNMORE SILT LOAM: III. INFLUENCE OF LONG-TIME FERTILITY TREATMENTS<sup>1</sup>

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The first paper of this series<sup>2</sup> reported that in plots treated yearly since 1914 with farmyard manure (horse dung) or with artificial fertilizers the whole soil and two aggregate-size groups contained more total and alkali-soluble organic matter than adjoining untreated plots. The manured plots contained more than those receiving artificials alone. Seasonal variations in the organic matter content of the aggregates were also noted. In the second paper of the series,<sup>3</sup> the whole soil and five aggregate-size groups were compared. There was evidence that some of the size groups were related, though differently as regards total and alkali-soluble organic matter. On the basis of alkali-soluble organic matter alone, the size groups were divided into two classes, those larger than 1.0 mm. and those smaller. In the present paper the study is extended for a full four-course rotation using the 1.0–2.0-mm. group as representative of the large aggregates and the 0.10–0.25-mm. group as representative of the small ones.

## RESULTS AND DISCUSSION

The data herein presented for the total and alkali-soluble organic matter in the whole soil and in large and small aggregates represent four sampling periods of 6, 18, 30, and 42 months after ground limestone had been applied to 96 plots in the spring of 1940. The data for the four sampling periods are presented in tables 1, 2, 5, and 6. The summaries of the analyses of variance and of covariance are presented in tables 3 and 4, respectively. Table 3 shows the significant effects at the 1 and 5 per cent levels of the experimental factors, for example, crops, series, periods, and treated plots vs. untreated plots. Table 4 shows the tests of significance after adjustment for the regressions as follows: (a) between alkali-soluble and total organic matter in the whole soil and in the soil aggregates, and (b) between the whole soil and soil aggregates in content

<sup>1</sup> Contribution from the Virginia Agricultural Experiment Station, Blacksburg, Virginia, and the Soil Conservation Service, U. S. Department of Agriculture. The author was formerly, soils technologist, Virginia Agricultural Experiment Station, and is now associate professor of soils, National Farm School and Junior College, Bucks County, Pennsylvania.

<sup>2</sup> Elson, J., and Azar, E. 1943 Distribution of total and alkali-soluble organic matter between the whole soil and soil aggregates of Dunmore silt loam: I. Influence of fertility treatments 6 and 18 months after liming. *Soil Sci.* 55: 177–183.

<sup>3</sup> Elson, J. 1943 Distribution of total and alkali-soluble organic matter between the whole soil and soil aggregates of Dunmore silt loam: II. Comparison of five aggregate-size groups 30 months after liming. *Soil Sci.* 56: 235–240.



of both alkali-soluble and total organic matter. It should be understood, for the regressions in table 4, that significance at the 1 or 5 per cent level shows a difference, whereas nonsignificance indicates a correlation. This point was previously discussed.<sup>3</sup>

TABLE 1

*Total organic matter in whole soil and in soil aggregates—summary of treatment comparison for treated vs. untreated plots and for manured vs. fertilized plots, by crops, by sampling periods, and by series of plots.\**

	WHOLE SOIL						LARGE AGGREGATES						SMALL AGGREGATES					
	Treatment comparison						Treatment comparison						Treatment comparison					
	Treated†	Untreated†	Difference	Manured‡	Fertilized‡	Difference	Treated	Untreated	Difference	Manured	Fertilized	Difference	Treated	Untreated	Difference	Manured	Fertilized	Difference
<i>Crops</i>																		
Corn.....	2.70	2.14	0.56	3.88	2.36	1.02	2.65	2.07	0.58	3.32	2.31	1.01	2.72	2.06	0.66	3.37	2.40	0.97
Wheat.....	2.70	2.18	0.52	3.27	2.41	0.86	2.62	2.11	0.51	3.15	2.36	0.79	2.70	2.11	0.59	3.24	2.43	0.81
Clover.....	2.71	2.19	0.52	3.28	2.42	0.86	2.62	2.13	0.49	3.16	2.34	0.82	2.68	2.14	0.54	3.22	2.40	0.82
Grass.....	2.72	2.19	0.53	3.33	2.42	0.91	2.66	2.11	0.55	3.24	2.37	0.87	2.73	2.13	0.60	3.34	2.42	0.92
<i>Sampling periods</i>																		
6 months....	2.73	2.19	0.54	3.35	2.42	0.93	2.67	2.17	0.50	3.25	2.38	0.87	2.75	2.14	0.61	3.34	2.45	0.89
18 months....	2.72	2.21	0.51	3.29	2.44	0.85	2.55	2.06	0.49	3.07	2.29	0.78	2.60	1.99	0.61	3.12	2.34	0.78
30 months....	2.70	2.17	0.53	3.27	2.42	0.85	2.68	2.12	0.56	3.28	2.39	0.89	2.79	2.16	0.63	3.35	2.51	0.84
42 months....	2.68	2.13	0.55	3.34	2.35	0.99	2.65	2.08	0.57	3.28	2.33	0.95	2.70	2.15	0.55	3.36	2.36	1.00
<i>Series of plots ¶</i>																		
I.....	2.84	2.11	0.73	3.72	2.41	1.31	2.81	2.07	0.74	3.51	2.46	1.05	2.78	2.02	0.76	3.71	2.32	1.39
II.....	2.68	2.33	0.35	3.31	2.37	0.94	2.58	2.28	0.30	3.14	2.31	0.83	2.68	2.24	0.44	3.22	2.41	0.81
III.....	2.69	2.30	0.39	3.16	2.45	0.71	2.56	2.12	0.44	3.09	2.29	0.80	2.73	2.28	0.45	3.12	2.53	0.59
IV.....	2.61	1.95	0.66	3.07	2.38	0.69	2.60	1.95	0.65	3.14	2.33	0.81	2.64	1.90	0.74	3.12	2.40	0.72

\* Results in percentage of dry matter.

† Data on treated plots represent the mean of 48 plots: 32 fertilized and 16 manured.

‡ Data on untreated plots represent the mean of 48 plots.

§ Data on manured plots represent the mean of 16 plots.

|| Data on fertilized plots represent the mean of 32 plots.

¶ For series of plots the means are for one-fourth the number of plots.

### *Total vs. alkali-soluble organic matter*

The tests of significance presented in table 4 indicate the relationship found between alkali-soluble and total organic matter in the whole soil and in the two aggregate-size groups. It is evident from the regressions that alkali-soluble closely followed total organic matter in the whole soil and in small aggregates. However, since this did not hold for the large aggregates, it is taken to mean that the accumulation of the alkali-soluble fraction in the large aggregates did not depend solely on the amount of total organic matter in this size group. Other factors such as fertilizer or manure treatments influenced the ratio of alkali-soluble to total organic matter in these aggregates.

*Total organic matter in the whole soil and aggregate-size groups*

The tests of significance in table 4 indicate little relationship between the two aggregate-size groups and the whole soil as regards total organic matter. Further, the two aggregate-size groups were less closely related to each other.

TABLE 2

*Alkali-soluble organic matter in whole soil and in soil aggregates—summary of treatment comparisons for treated vs. untreated plots, and for manured vs. fertilized plots, by crops, by sampling periods, and by series of plots\**

	WHOLE SOIL						LARGE AGGREGATES						SMALL AGGREGATES					
	Treatment comparison						Treatment comparison						Treatment comparison					
	Treated†	Untreated†	Difference	Manured‡	Fertilized‡	Difference	Treated	Untreated	Difference	Manured	Fertilized	Difference	Treated	Untreated	Difference	Manured	Fertilized	Difference
<i>Crops</i>																		
Corn.....	1.53	1.23	0.30	1.92	1.33	0.59	1.55	1.20	0.35	1.88	1.38	0.50	1.54	1.17	0.37	1.90	1.37	0.53
Wheat.....	1.53	1.25	0.28	1.88	1.36	0.52	1.50	1.27	0.23	1.78	1.37	0.39	1.56	1.21	0.35	1.86	1.41	0.45
Clover.....	1.56	1.26	0.30	1.88	1.39	0.49	1.56	1.26	0.30	1.86	1.41	0.45	1.56	1.23	0.33	1.83	1.40	0.43
Grass.....	1.55	1.26	0.29	1.94	1.35	0.59	1.52	1.23	0.29	1.80	1.39	0.41	1.63	1.27	0.36	2.04	1.43	0.61
<i>Sampling periods</i>																		
6 months.....	1.55	1.24	0.31	1.97	1.34	0.63	1.56	1.24	0.32	1.91	1.39	0.52	1.47	1.16	0.31	1.77	1.32	0.45
18 months....	1.47	1.21	0.26	1.80	1.30	0.50	1.46	1.21	0.25	1.74	1.32	0.42	1.44	1.13	0.31	1.74	1.28	0.46
30 months....	1.43	1.17	0.26	1.74	1.23	0.49	1.46	1.16	0.30	1.66	1.36	0.30	1.59	1.21	0.38	1.92	1.43	0.49
42 months....	1.71	1.38	0.33	2.12	1.50	0.62	1.64	1.35	0.29	1.98	1.48	0.50	1.80	1.38	0.42	2.25	1.57	0.68
<i>Series of plots ¶</i>																		
I.....	1.54	1.17	0.37	2.04	1.29	0.75	1.60	1.23	0.37	1.98	1.40	0.58	1.56	1.11	0.45	2.08	1.29	0.79
II.....	1.52	1.37	0.15	1.88	1.33	0.55	1.50	1.36	0.14	1.78	1.36	0.42	1.59	1.35	0.24	1.98	1.42	0.51
III.....	1.56	1.34	0.22	1.83	1.43	0.40	1.50	1.24	0.26	1.73	1.38	0.35	1.58	1.31	0.27	1.79	1.48	0.31
IV.....	1.55	1.13	0.42	1.83	1.38	0.50	1.54	1.14	0.40	1.79	1.41	0.38	1.57	1.10	0.47	1.88	1.41	0.47

\* Results in percentage of dry matter.

† Data on treated plots represent the mean of 48 plots: 32 fertilized and 16 manured.

‡ Data on untreated plots represent the mean of 48 plots.

§ Data on manured plots represent the mean of 16 plots.

¶ Data on fertilized plots represent the mean of 32 plots.

¶ For series of plots the means are for one-fourth the number of plots.

These findings are of interest because it is recognized that the organic matter found in the aggregates originally was present in the whole soil. Evidently, in the formation of the aggregates the distribution of the organic matter between the whole soil and the aggregates depended on other experimental factors besides the total amount of organic matter in the soil. This point is of significance because there was little difference in the average organic matter content of the soil and soil aggregates (table 6). From these results it may be concluded that the incorporation of organic matter in the soil will not necessarily result in an even distribution of the material between the soil and soil aggregates.

*Alkali-soluble organic matter in the whole soil and aggregate-size groups*

The tests of significance shown in table 4 indicate little relationship between the whole soil and the two aggregate-size groups and between the two size groups as regards alkali-soluble organic matter. This was to be expected since alkali-soluble was found to be closely related to total organic matter, and the preceding discussion showed that there was little relationship in the organic matter content of the whole soil and that of the aggregate-size groups.

TABLE 3

*Summaries of analyses of variance of total and alkali-soluble organic matter data*

	DEGREES OF FREEDOM	MEAN SQUARES					
		Total organic matter			Alkali-soluble organic matter		
		Whole soil	Aggregates		Whole soil	Aggregates	
			Large	Small		Large	Small
Crops.....	3	0.0256	0.0135	0.0186	0.0164	0.0253	0.1458
Sampling periods.....	3	0.0684	0.2677**	0.6247**	1.0851**	0.6443**	1.8185**
Series.....	3	1.0760**	0.6040**	0.9534**	0.3042**	0.1515	0.5135**
Error (a).....	6	0.0556	0.0234	0.0409	0.0273	0.0436	0.0668
Treated vs. untreated.	1	27.2267**	27.0300**	34.4162**	8.0678**	8.1288**	12.0346**
By crops.....	3	0.0134	0.0368	0.0541	0.0011	0.0503	0.0084
By periods.....	3	0.0047	0.0428	0.0350	0.2254	0.0222	0.0707
By series.....	3	0.8853**	0.9384**	0.7490**	0.3777**	0.3253**	0.3422**
Error (b).....	6	0.0204	0.0718	0.0251	0.0100	0.0333	0.0186
Fertilizer treatment							
N.....	1	0.1575*	0.0058	0.4039**	0.0059	0.3220**	0.0756
P.....	1	1.2462**	0.1225	3.1658**	0.1632*	0.1891*	1.1571**
K.....	1	0.3972**	0.3062*	1.0970**	0.2024*	0.0004	0.2186*
NP.....	1	0.0328	0.0536	0.0056	0.0004	0.0420	0.1158
KP.....	1	0.7828**	0.3342**	1.7414**	0.4198**	0.3160**	0.2547*
NK.....	1	0.0107	0.5565**	0.8080**	0.0000	0.1391*	0.1294
NPK.....	1	0.5927**	1.3041**	0.1853	0.2729**	0.3698**	0.3071**
Manure treatment....	3	0.2450**	0.2637**	0.1788*	0.0764	0.1315**	0.1412*
Manured vs. fertilized.	1	35.2898**	32.4686**	32.8360**	12.9323**	7.9868**	11.5613**
By crops.....	3	0.0661	0.0922	0.0634	0.0296	0.0287	0.0506
By periods.....	3	0.0496	0.0477	0.0940	0.0770	0.1130*	0.1190*
By series.....	3	0.8890**	0.1495**	1.3275**	0.2347**	0.1138*	0.4155**
Error (c).....	156	0.0399	0.0514	0.0546	0.0352	0.0320	0.0399
Untreated.....	176	0.1376	0.1220	0.1536	0.0721	0.0651	0.0751
Total.....	383						

\* Significant at 5% level

\*\* Significant at 1% level.

*Effect of fertilizer treatments on total and alkali-soluble organic matter  
in the whole soil and soil aggregates*

Table 5 summarizes the main effects and interactions of the fertilizer elements N, P, and K on total and alkali-soluble organic matter. It is recognized that

these elements, singly or in combination, had on organic matter an indirect influence which was related to the effect these artificials had on crop growth. The sources of soil organic matter consisted of the roots of crops, weeds, and crop residues turned under in the course of cultivation. It should be noted that an

TABLE 4

*Summaries of tests of significance resulting from covariance analyses of total and alkali-soluble organic matter data*

	DE- GREES OF FREE- DOM	ADJUSTED FOR REGRESSION OF ALKALI-SOLUBLE ON TOTAL ORGANIC MATTER			TOTAL ORGANIC MATTER			ALKALI-SOLUBLE ORGANIC MATTER		
		Whole Soil	Large aggre- gates	Small aggre- gates	Adjusted for regression of:			Adjusted for regression of:		
					Large aggre- gates on whole soil	Small aggre- gates on whole soil	Small on large aggre- gates	Large aggre- gates on whole soil	Small aggre- gates on whole soil	Small on large aggre- gates
Crops.....	3	..	..	..	..	..	..	..	..	.
Periods.....	3	**	**	**	**	**	..	..	**	**
Series.....	3	..	..	..	**	*	**	**	..	**
Error (a).....	6									
Treated vs. untreated.	1	..	..	..	..	..	**	..	..	*
By crops.....	3	..	..	..	..	..	..	..	..	..
By periods.....	3	..	..	..	..	..	..	..	**	..
By series.....	3	**	..	..	..	..	..	..	..	..
Error (b).....	6									
Fertilizer treatment										
N.....	1	..	**	..	**	..	**	*	..	**
P.....	1	..	*	..	**	**	**	..	**	**
K.....	1	..	**	..	..	**	**	..	..	*
NP.....	1	..	..	**	..	..	..	..	*	..
KP.....	1	..	..	..	**	**	**	..	..	..
NK.....	1	..	..	..	**	**	**	*	*	**
NPK.....	1	..	..	*	**	..	*	*	..	..
Manure treatment....	3	..	**	..	**	*	..	*	*	..
Manured vs. fertilized.	1	..	**	..	..	..	**	**	**	**
By crops.....	3	..	..	..	..	..	..	..	..	..
By periods.....	3	..	**	..	..	..	..	..	*	*
By series.....	3	..	..	..	**	**	**	..	**	**
Error (c).....	156									

.. Nonsignificant.

\* Significant at 5 per cent level.

\*\* Significant at 1 per cent level.

increase or decrease in total or alkali-soluble organic matter in the whole soil was followed by a similar effect on the small aggregates. This did not always hold for the large-size group. The significant increases or decreases shown in table 5 were not of great magnitude, but they indicated the long-time trend, since the fertilizers had been applied since 1914.

TABLE 5

*Summary of main effects and interactions of fertilizer elements on total and alkali-soluble organic matter content of whole soil and soil aggregates†*

	TOTAL ORGANIC MATTER			ALKALI-SOLUBLE ORGANIC MATTER		
	Whole soil	Aggregates		Whole soil	Aggregates	
		Large	Small		Large	Small
N.....	-0.035*	+0.007	-0.056**	-0.007	+0.050**	-0.024
P.....	+0.100**	+0.031	+0.157**	+0.036*	+0.038*	+0.095**
K.....	+0.056**	+0.049*	+0.092**	+0.040*	+0.002	+0.041*
NP.....	-0.016	-0.020	+0.007	+0.002	-0.018	-0.030
KP.....	+0.078**	+0.051**	+0.117**	+0.057**	+0.050**	+0.045*
NK.....	+0.009	-0.066**	+0.079**	+0.000	-0.033*	+0.032
NPK.....	-0.068**	-0.101**	-0.038	-0.046**	-0.054**	-0.049**

† Results in percentage of dry matter.

\* Significant at 5 per cent level.

\*\* Significant at 1 per cent level.

TABLE 6

*Summary of treatment comparisons for treated vs. untreated plots and for manured vs. fertilized plots for total and alkali-soluble organic matter in whole soil and soil aggregates\**

	TREATED†	UN-TREATED‡	DIF-FERENCE§	MA-NURED§	FERTI-LIZED	DIF-FERENCE	CORREC-TION¶	COR-RECTED DIFFER-ENCE**
<i>Total organic matter</i>								
Whole soil.....	2.71	2.17	0.54	3.31	2.40	0.91	0.51	0.40
Large aggregates.....	2.64	2.11	0.53	3.22	2.35	0.87	0.42	0.45
Small aggregates.....	2.71	2.11	0.60	3.29	2.42	0.87	0.45	0.42
<i>Alkali-soluble organic matter</i>								
Whole soil.....	1.54	1.25	0.29	1.91	1.36	0.55	0.37	0.18
Large aggregates.....	1.53	1.24	0.29	1.82	1.39	0.43	0.26	0.17
Small aggregates.....	1.57	1.22	0.35	1.92	1.40	0.52	0.32	0.20

\* Results in percentage of dry matter. All plots sampled in 4 successive years.

† Mean of 48 plots; 32 fertilized and 16 manured; 192 samples.

‡ Mean of 48 plots; 192 samples.

§ Mean of 16 plots; 64 samples.

|| Mean of 32 plots; 128 samples.

¶ Average difference in total or alkali-soluble organic matter between untreated plots adjoining manured plots and untreated plots adjoining fertilized plots.

\*\* Corrected difference equals difference between the two preceding columns.

*Treatment comparisons for total and alkali-soluble organic matter in whole soil and soil aggregates*

Table 6 summarizes the treatment comparisons for total and alkali-soluble organic matter in the whole soil and in soil aggregates. The soil and aggregate-size groups from the treated plots contained about 25 per cent more organic

matter than the samples from the untreated ones. It should be remembered that in the layout of the experiment each treated plot was located next to an untreated one, which helped to rule out soil differences between the treated and the untreated plots. Before a similar comparison could be made between the manured and the fertilized plots, a correction factor had to be calculated. This was necessary because the treatments were not randomized over the experimental area. The correction was an inherent soil fertility factor and was calculated as the average difference between the untreated plots adjoining the manured ones and the untreated plots adjoining the fertilized ones. The correction was subtracted from the difference between the manured and the fertilized plots to give a corrected difference. After this correction was made it was found that the soil and soil aggregates from the manured plots contained 15 per cent more total or alkali-soluble organic matter than the samples from the fertilized plots. This difference amounted to 4 tons of total organic matter per acre<sup>4</sup> and is not considerable when it is recalled that 112 tons of manure per acre had been applied in seven 4-year rotations (1914-1942). Much of the added manure had been mineralized and used up in plant growth, which resulted in larger crop yields from the manured plots.

#### SUMMARY

Total organic matter and alkali-soluble organic matter were determined on the whole soil and on large and small aggregates (1.0-2.0 mm. and 0.10-0.25 mm. respectively) separated from the soil of 96 long-time fertility plots on Dunmore silt loam 6, 18, 30, and 42 months after liming.

Whole soil and both aggregate-size groups from the treated plots (manured or fertilized) contained 25 per cent more total and alkali-soluble organic matter than the untreated ones, and the manured plots contained 15 per cent more than the fertilized ones. The latter difference amounted to 4 tons of total organic matter per acre and was inconsiderable after 112 tons per acre of manure had been applied over a 28-year period.

The distribution of alkali-soluble matter followed that of total organic matter in the whole soil and in small aggregates. This did not hold for the large aggregates.

The distribution of total organic matter between the aggregate-size groups and whole soil depended on other experimental factors than the amount of organic matter. Further, the two aggregate-size groups were not related to each other. The same relationship was found for alkali-soluble organic matter.

The main effects and interactions of the fertilizer elements N, P, and K on total and alkali-soluble organic matter in the soil and in aggregate-size groups are summarized. It was noted that an increase or decrease of these materials in the whole soil resulted in a corresponding effect on the small aggregates. This did not always hold for the large aggregates.

<sup>4</sup> This is calculated on the basis of 1,000 tons of soil per acre to plow depth.



# FIXATION OF POTASSIUM IN RELATION TO EXCHANGE CAPACITY OF SOILS: IV. EVIDENCE OF FIXATION THROUGH THE EXCHANGE COMPLEX<sup>1</sup>

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The experiments reported in the previous papers<sup>3</sup> of this series demonstrated a definite relation between the exchange complex and K fixation. As more or less K is permitted to enter the exchange complex, so more or less K is fixed in the nonreplaceable state. For further insight into this relationship a quantitative study was undertaken.

## EXCHANGE COMPLEX AND FIXATION

Duplicate 5-gm. samples of Montalto hydrogen colloid (2  $\mu$  and smaller, organic-matter-free, cation-exchange capacity 0.43 m.e. per gram) were used for this work. To separate sets were added respectively 0.5, 1.00, 2.00, 3.50, 5.00, 10.00, 15.00, 20.00, 25.00, and 50.00 ml. of 0.1246 N KCl solution. To another set was added 15.00 ml of KCl solution containing 2.65 mgm. K per milliliter. The samples were then alternately wetted and dried to induce K fixation in the manner reported in paper I of this series.

After fixation, the samples were taken up with water, filtered, and washed until free from water-soluble K. The quantity of water-soluble K was then determined on the filtrates. After the water extraction the samples were leached with 0.05 N HCl and the exchangeable K was determined. The exchange capacities of the residues were determined by the barium acetate method.

Results appear in table 16 and in figures 1, 2, 3, and 4. Column 2 of table 16 is calculated by subtracting the water-extractable K from the total added. The validity of this calculation is based on evidence presented in the earlier papers. It is assumed that the K which was fixed was once in the exchange complex. Reduction in exchange capacity (column 4, table 16) was obtained by subtracting the exchange capacity after fixation from the exchange capacity after merely repeated wetting and drying. The data indicate respectively the following relationships: first, the total quantity of K added and the quantity fixed; second, the quantity of K added and the quantity that entered the exchange complex; third, the quantity of K that entered the exchange complex and the quantity fixed; and fourth, the quantity of K fixed and the decrease in exchange capacity due to fixation.

Specifically, table 16 shows that with increasing K applications, increasing

<sup>1</sup> Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

<sup>2</sup> Temporarily withdrawn; resubmitted December 16, 1946.

<sup>3</sup> Joffe, J. S., and Levine, A. K. Fixation of potassium in relation to exchange capacity of soils: I, II, III. *Soil Sci.* 62: 411-420, 1946; 63: 151-158, 1947.



quantities of K are fixed. The relationship between these variables is expressed in figure 1. Two graphs are given, both of which exhibit the same data. One curve, the "flatter" one, is plotted with ordinates and abscissas of equal weight. This curve permits direct comparison without regard to scale, and emphasizes the actual trend of the data. From it we readily note that although fixation increases with increase in K applied, the *rate* of increase falls off as the K additions grow larger. This behavior indicates some underlying factor which tends to limit fixation.

For closer examination of the results another curve has been constructed with the ordinate five times the abscissa. This graph shows that although the increase in fixation with K addition is monotonic, the *rate of change* of increase of K fixation with application reaches a maximum at some point intermediate

TABLE 16  
*Relation of K applied to amount entering exchange complex and to amount fixed\**

AMOUNT OF K ADDED	AMOUNT OF K WHICH ENTERED EXCHANGE COMPLEX	AMOUNT OF K FIXED	REDUCTION IN EXCHANGE CAPACITY
<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
0.062	0.062	0.042	0.013
0.125	0.114	0.053	0.065
0.249	0.170	0.064	0.074
0.436	0.306	0.149	0.137
0.623	0.394	0.187	0.162
1.016	0.635	0.300	0.236
1.246	0.736	0.337	0.242
1.869	1.052	0.514	0.307
2.492	1.107	0.551	0.320
3.115	1.155	0.552	0.314
6.230	1.514	0.820	0.355

\* Aqueous KCl added to Montalto H-colloid.

on the curve. It is significant that this critical point turns out to be about the quantity of K fixed when the amount of K added is equal to the exchange capacity of the colloid.

The existence of this critical point emphasizes the relation between fixation and the exchange complex. When a small quantity (that is, small relative to the exchange capacity) of K is applied, the capacity of the exchange complex is not a limiting factor and a large *proportion* of the K enters into exchange. When the quantity of applied K is increased beyond the exchange capacity, however, the *proportion* which can enter the complex becomes smaller; hence, though the absolute quantity of fixation increases, it does so at a *decreasing rate*.

The work of Volk<sup>4</sup> and that of Shaw and MacIntire<sup>5</sup> are in agreement with

<sup>4</sup> Volk, N. J. Fixation of potash in difficultly available form in soils. *Soil Sci.* 37: 267-287. 1934.

<sup>5</sup> Shaw, W. M., and MacIntire, W. H. Relationship between water soluble, replaceable and fixed fractions of potash additions to soils. *Soil Sci. Soc. Amer. Proc.* 1: 143-148. 1936.

the foregoing. Volk got a monotonic curve similar to that in figure 1. He did not, however, explain his results. Shaw and MacIntire, working with a Cherokee clay subsoil and a black calcareous loam, found that a higher percentage of K was fixed when the K application was small than in the case of a larger application.

For further analysis, the amount of K which entered the complex was plotted against K applied. Figure 2, which exhibits this relationship, completely verifies the deductions made from figure 1. The amount of K which enters the exchange complex increases almost linearly with application until the application is almost equivalent to the exchange capacity; after that it falls off markedly. Again there is the same critical point on the curve; that is, there is a maximum in the *rate of change* of entry of K into the exchange complex, and this maximum occurs (approximately) at the equivalence point.

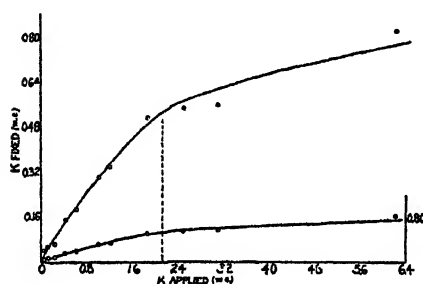


FIG. 1

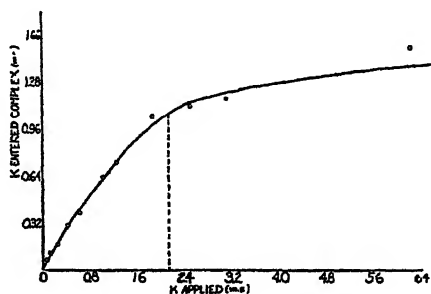


FIG. 2

FIG. 1. FIXATION OF POTASSIUM AS A FUNCTION OF QUANTITY APPLIED

System: 0.1246N KCl and 5.000 gm. Montalto hydrogen colloid

FIG. 2. EXCHANGE OF POTASSIUM AS A FUNCTION OF QUANTITY APPLIED

System: 0.1246N KCl and 5.000 gm. Montalto hydrogen colloid

Figure 3 is foreshadowed by the discussion of the previous graphs. The linear relationship between the K which enters the complex and that fixed is very significant. It shows directly that K fixation is related to the exchange property and most strongly indicates that K must be in the exchange complex before it can be fixed. The slope of the line shows that somewhat under 50 per cent of the K which entered the complex was fixed. The possible significance of the slope will be discussed when the succeeding experiment is presented.

The reduction in exchange capacity after fixation is plotted against K fixed in figure 4. From this graph it is apparent that with increasing fixation the decrease in exchange capacity becomes larger. The reduction of the exchange capacity is not very regular, although there is a definite trend. The greatest rate of change of this curve occurs somewhat below the point that denotes the quantity fixed when an amount of K equal to the exchange capacity of the colloid is added. Speculation as to whether this has any significance is not ventured, principally because the precision with which the exchange capacities after fixation were determined does not warrant too close an examination.

It might have been expected, were there no data on hand to show the contrary, that decrease in exchange capacity and  $K$  fixed would vary linearly; why this is not the case has not been investigated. Of interest in figure 4 is the fact that a portion of the curve indicates a reduction in exchange capacity exceeding the quantity of  $K$  fixed. The curve then passes through a point where the fixation of  $K$  and the reduction in the exchange capacity are equal. This point occurs when almost 0.1 m.e.  $K$  is fixed. Beyond this point the reduction in exchange capacity is always less than the quantity of  $K$  fixed. The equivalence between fixation and reduction in exchange capacity reported by Truog and Jones<sup>6</sup> may possibly be explained on the basis of figure 4.

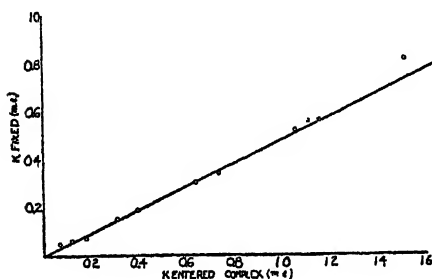


FIG. 3

FIG. 3. FIXATION OF POTASSIUM AS A FUNCTION OF QUANTITY ENTERING EXCHANGE COMPLEX

System: 0.1246*N* KCl and 5.000 gm. Montalto hydrogen colloid

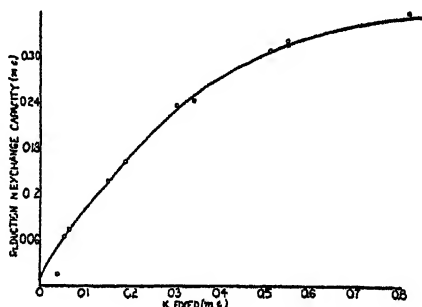


FIG. 4

FIG. 4. REDUCTION OF EXCHANGE CAPACITY OF MONTALTO COLLOID AS A FUNCTION OF THE QUANTITY OF POTASSIUM FIXED BY IT

#### FIXATION REACTIONS IN ALCOHOLIC SOLUTION

To test the scope and generality of the conclusions drawn, the experiment was repeated but with some very important modifications. Instead of the Montalto hydrogen colloid, hydrogen-saturated Wyoming bentonite was employed. In addition to this change, the fixation reaction was carried out in alcoholic solution, and  $K$  was applied as the acetate. Substitution of alcoholic  $K$ -acetate for aqueous  $KCl$  was intended to increase the magnitude of fixation. The range of  $K$  applications was also increased to more than four times that in the previous experiment. In order to maintain some basis for comparison with the previous experiment, quantities of hydrogen bentonite equivalent, on the basis of exchange capacity, to the Montalto hydrogen colloid were used.

Duplicate 2.700-gm. samples of hydrogen bentonite were employed: 2.700 gm. of the bentonite (exchange capacity, 0.79 m.e. per gram) was approximately equivalent to 5 gm. of Montalto colloid. To separate samples of the bentonite,

<sup>6</sup> Truog, E., and Jones, J. R. Fate of soluble potash applied to soils. *Indus. and Engin. Chem.* 30: 882-886. 1938.

1.00, 2.50, 5.00, 10.00, 15.00, 20.00, 30.00, 100.00, and 200.00 ml. of alcoholic K-acetate (1 ml. = 5.07 mgm. K) were added respectively. Fixation was then induced as previously described. After fixation, the samples were taken up in alcohol, thrown on filters, and leached. The samples were then washed with cold 0.1 *N* alcoholic HCl to remove the exchangeable K. Both the alcohol and the alcoholic acid filtrates were kept separate and analyzed for K. The exchange capacity after fixation was also determined. Results are shown in table 17 and in figures 5, 6, and 7.

In table 17, as in the previous table, column 2, the amount of K which entered the exchange complex, was calculated by subtracting the alcohol-extractable K from the quantity originally added. The reduction in exchange capacity was determined by subtracting the exchange capacity after fixation from the

TABLE 17

*Relation of K applied to amount entering exchange complex and to amount fixed\**

AMOUNT OF K ADDED	AMOUNT OF K WHICH ENTERED EXCHANGE COMPLEX	AMOUNT OF K FIXED	REDUCTION IN EXCHANGE CAPACITY
<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>	<i>m.e.</i>
0.130	0.130	0.064	0.048
0.324	0.324	0.155	0.109
0.648	0.648	0.338	0.117
1.297	1.167	0.554	0.133
1.945	1.616	0.695	0.134
2.593	1.933	0.823	0.145
3.800	2.241	0.940	0.142
12.971	3.232	1.356	0.176
25.934	4.012	1.726	0.184

\* Alcoholic AcOK added to H-bentonite.

exchange capacity of an equal sample of bentonite which had previously been repeatedly wetted with alcohol and dried.

Very striking is the similarity between figure 5 and figure 1. Both curves are of the same general shape and have like characteristics, although it should be noted that figure 5 covers an enormous range of K addition. Two graphs appear in figure 5, and both represent the same data. As before, one graph is plotted so that the ordinates are equal in weight to the abscissas, whereas in the other the ordinates are expanded.

The "flatter" curve in figure 5 shows at a glance that K fixation increases with increasing application. As the magnitude of the K additions becomes greater, however, the rate of increase of fixation falls off rapidly. Very noteworthy is the fact that even with the greatest applications of K, fixation is still far below the exchanged capacity; that is, the K fixed is in every case less than the quantity which is able to enter the exchange complex. Thus even when 25.934 m.e. K was added to hydrogen bentonite having a total exchange capacity of 2.133 m.e., the fixation was only 1.726 m.e., a quantity appreciably below

the exchange capacity. In a subsequent experiment, a much larger quantity of K was applied under the same conditions, and still the fixation was far short of 2.133 m.e., the exchange capacity. These considerations lead to the belief that an upper boundary to fixation is approached as the K applications become increasingly great. The broken line parallel to the abscissa in figure 5 indicates K fixation equal to the exchange capacity. It is evident that this value is never reached by the curve and that it is an upper boundary of that curve. Whether

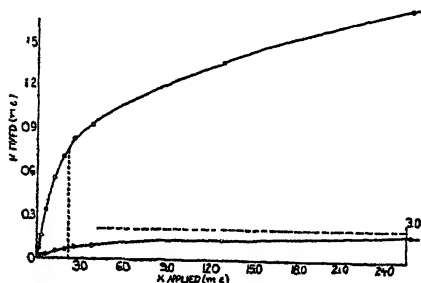


FIG. 5

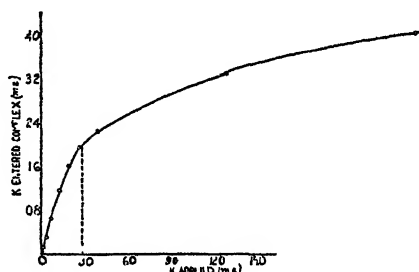


FIG. 6

FIG. 5. FIXATION OF POTASSIUM AS A FUNCTION OF QUANTITY APPLIED  
System: alcoholic  $\text{CH}_3\text{COOK}$  (1ml. = 5.07 mgm. K) and 2.700 gm. hydrogen bentonite

FIG. 6. EXCHANGE OF POTASSIUM AS A FUNCTION OF QUANTITY APPLIED  
System: alcoholic  $\text{CH}_3\text{COOK}$  (1 ml. = 5.07 mgm. K) and 2.700 gm. hydrogen bentonite

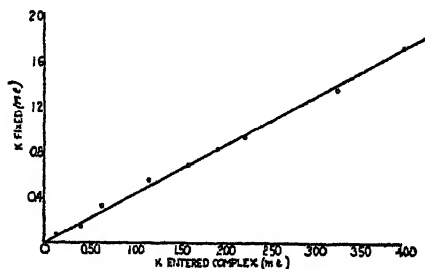


FIG. 7. FIXATION OF POTASSIUM AS A FUNCTION OF QUANTITY ENTERING EXCHANGE COMPLEX

System: alcoholic  $\text{CH}_3\text{COOK}$  (1 ml. = 5.07 mgm. K) and 2.700 gm. hydrogen bentonite

it is the least upper boundary (or asymptote) is not known. It may be that there is an upper boundary to fixation closer than the broken line in question. In any case, fixation cannot be greater than the exchange capacity. This conclusion holds also, of course, for the experiment with Montalto colloid as described in figure 1; in that case, however, the fixation did not approach the exchange capacity nearly so closely as in the bentonite experiment.

The other curve in figure 5 was drawn with expanded ordinates to permit closer examination of its properties. The significant thing here is that the

maximum in the rate of change of increase in fixation with addition—the maximum in the second derivative of a theoretical curve—occurs, just as in figure 1, very nearly at the point where an application equal to the exchange capacity is made. Since this maximum occurs at the same point in both experiments, the point certainly is critical and has significance independent of the material employed as the fixing agent.

Figure 6 illustrates the relationship between the K applied and that entering the exchange complex. Again, as in figure 2, the amount which enters the complex increases with increasing K application, although the increase is at a decreasing rate. Once more, the maximum in the *rate of change* of increase of entry with application is at a point equivalent to the exchange capacity. That the ordinates are roughly twice the ordinates in figure 5 indicates a straight-line relationship between the quantity measured along the ordinates of both graphs.

This linear relationship, between K entering the exchange complex and the quantity fixed, is exhibited in figure 7. This not only substantiates the linear relationship determined in the work with Montalto colloid (fig. 3), but definitely furthers its implications. For one thing, the straight-line relation was determined over a far wider range in this instance where bentonite was used, and indicates that the relationship found is not a linear-like portion of a curve with gradual change in slope, but rather that it is a true straight line. For another thing, the slope of the line in figure 7 is very nearly equal to that in figure 3. From the slope we see that 48 per cent of the K which enters the complex of the Montalto hydrogen colloid is fixed, whereas in the case of hydrogen bentonite 43 per cent is fixed (under laboratory conditions which induce maximum fixation).

Table 17 gives the reduction in exchange capacity due to fixation. There is a general increase in the magnitude of the reduction of the exchange capacity with increasing fixation, but there appears to be no regularity. There is no doubt, however, that fixation has some effect on the ability of a material to exchange cations.

#### CONCLUSIONS

In the two experiments described, a simple linear relationship was found between the amount of K entering the exchange complex and that fixed. The theory that K must first be in exchangeable form to be fixed is substantiated almost beyond question. The two experiments also indicate, through the similarity of the results obtained in each case, that the phenomenon of fixation is essentially the same for different fixing materials.



# A MODIFIED APPARATUS FOR LEACHING SOILS

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Before a series of determinations of exchangeable bases was undertaken, experiments were carried out with both the types of leaching apparatus described by Schollenberger and Simon.<sup>2</sup> The object was to decide which was the more suitable for routine use. It soon became evident that, though the larger apparatus had several important advantages (notably a closed air system), it was inferior to the smaller in simplicity of routine operation and in compactness. This paper describes an apparatus designed to combine the desirable features of both. It has been found to work excellently and to give values for total exchangeable bases, exchangeable hydrogen, and individual cations in close agreement with those obtained with Schollenberger and Simon's larger apparatus.

The general setup is shown in figure 1. The dimensions given are suitable for extracting 35 gm. of soil with 350 ml. of leaching solution. This volume of extract was found to be ample for all ordinary base-exchange analyses and to be relatively economical in material.

The whole success of the apparatus depends on the constant-level device, which, so far as the writer is aware, has not been described previously. It is shown in detail in figure 2 and its mode of action is as follows: As the level of liquid in the percolation tube falls, the difference in height  $x$  increases until the weight of the column of liquid below hole 1 is sufficient to break down the surface tension across this hole. When this occurs, air enters by hole 1, and liquid is released through hole 2 in an upward direction, thus replenishing the liquid in the percolation tube without disturbing the portion in contact with the soil. As the level in the percolation tube rises, the difference in height  $x$  is reduced below that necessary to break the surface tension across hole 1, and the outflow of liquid will stop until the cycle repeats itself as the liquid in the percolation tube gradually escapes through the soil. It will be seen that the action of hole 1 in supporting a column of liquid is analogous to that of a capillary tube. The same formula appears to apply in both cases ( $x = \frac{2T}{g\rho r}$ , where  $T$  = surface tension,  $\rho$  = density,  $r$  = radius of hole 1, and  $g$  = gravitational constant) and has been found useful for rough calculations before a con-

<sup>1</sup> Soil chemist, Cinchona Research Organisation, Amani, Tanganyika Territory. The author is indebted to D. W. Duthie, soil chemist, East African Agricultural Research Station, for his keen interest in the progress of the experimental work and for many interesting and helpful discussions.

<sup>2</sup> Schollenberger, C. J., and Simon, R. H. 1945 Determination of exchange capacity and exchangeable bases in soil-ammonium acetate method. *Soil Sci.* 59: 13-24.



stant-level tube is made. It is important that hole 2 be not too large; if it is, a surge of liquid will occur when air enters by hole 1, with the result that the level in the percolation tube rises considerably above its minimum before the

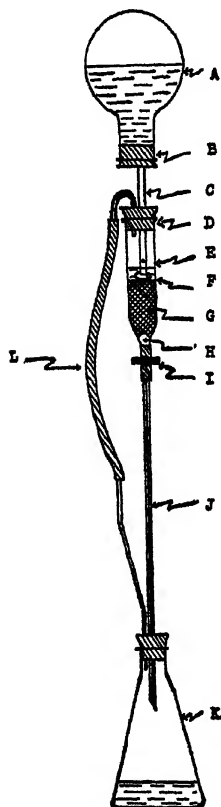


FIG. 1

FIG. 1. GENERAL SETUP OF SOIL-LEACHING APPARATUS

A, reservoir flask (400-450 ml.); B, rubber stopper; C, constant-level tube; D, cork or rubber stopper; E, percolation tube (12 by 3 cm.); F, filter paper; G, soil; H, cotton wool plug; I, screw clamp; J, wide-bore capillary tube; K, receiving flask (500 ml.); L, air return tube. Scale of diagram,  $\frac{1}{4}$  inch equals approximately 1 inch.

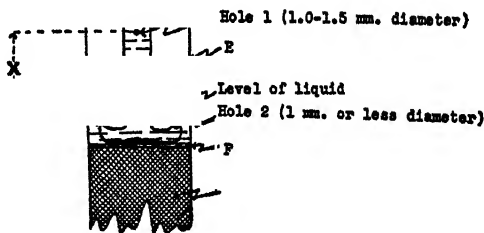


FIG. 2

FIG. 2. DETAILED CONSTRUCTION OF CONSTANT-LEVEL DEVICE

A, reservoir flask; B, rubber stopper; C, constant-level tube (12-14 cm. long, 8 mm. bore); D, cork or rubber stopper; E, percolation tube; F, filter paper; G, soil. Diagram drawn to half scale.

re-establishment of a surface at hole 1 can check the flow. When hole 1 has a diameter of about 1 mm. and hole 2 is small (1 mm. or less), hole 1 is always about 2 cm. above the level of the liquid in the percolation tube, and consequently the movement of liquid in the lower part of the constant-level tube (below hole

1) is always downward and undisturbed by the movement of air bubbles. Under these conditions it is theoretically impossible for any solution in the percolation tube to be carried back to the reservoir; and that no mixing takes place was demonstrated practically by operating the device with water in the reservoir and permanganate solution in the percolation tube.

The apparatus can be assembled as follows (see figure 1):

1. Thirty-five grams of soil is introduced into the percolation tube, fitted with a pad of cotton wool as described by Schollenberger and Simon. The writer has found it advantageous to cover the top of the soil with a disc of filter paper (*F*) which serves to prevent the soil from being churned up when the leaching solution is first introduced. The filter paper is held in place by the flat bottom of the constant-level tube when the latter is inserted, and a preparatory adjustment is made by merely sliding the tube up and down through cork *D*.

2. The percolation tube is attached to its support and capillary tube *J* and receiver *H* are fitted.

3. Next, 350 ml. of leaching solution is measured into flask *A*, and rubber stopper *B*, complete with constant-level tube, and cork *D*, are inserted.

4. The end of the constant-level tube is next brought over the open end of the percolation tube and lowered into it while flask *A* is being inserted. Cork *D* is pressed home, and the system is closed by connecting rubber tube *L*.

The screw clamp *I* is left open until air has been displaced downward by the leaching solution when, if it is desired to soak the soil before leaching, the clip is closed or, if immediate percolation is required, adjusted to a suitable rate of percolation.

The apparatus described is considered to embody the following advantages:

1. It employs a closed air system and, accordingly, Brown's<sup>\*</sup> method for exchangeable hydrogen can be applied to ammonium acetate extracts.

2. The leaching system employed prevents transfer of material dissolved from the soil to the reservoir of leaching solution.

3. The apparatus employs a constant-level device and so requires no adjustment apart from setting the screw clamp to the required speed of percolation.

4. As all the air in the circulating system is at atmospheric pressure, the necessity for completely air-tight joints in cork *D* does not arise.

5. The use of a wide-bore capillary tube at *J* (fig. 1) ensures the formation of an unbroken liquid column and assists percolation by suction. As the suction is independent of the height of liquid in the reservoir, the rate of percolation remains steady and does not fall off as the leaching proceeds.

6. The apparatus is easy to assemble, dismantle, and clean.

7. The apparatus is economical in space. One unit can be mounted on a single retort stand or, alternatively, a battery can be accommodated on simple wooden shelves fixed to the wall at the back of the bench. This arrangement uses scarcely any useful bench space, and each unit occupies a vertical strip of wall only 6 inches wide.

In conclusion, and for the benefit of amateur glass blowers (of whom the writer is one), the production of constant-level tubes is not difficult. The actual operations are as follows:

<sup>\*</sup> Brown, I. C. 1943 A rapid method of determining exchangeable hydrogen and total exchangeable bases of soils. *Soil Sci.* 56: 353-357.

1. A suitable piece of glass tubing (about 8 mm. internal diameter) is sealed at one end and a bulb is blown.
2. The bottom of this bulb is heated gently and flattened by pressing on a sheet of asbestos board.
3. The top of the bulb is next heated gently and uniformly and the tube telescoped into it by again pressing on the asbestos.
4. Hole 1 is blown.
5. Hole 2 is blown. It may be noted that if hole 1 is about 1 mm. in diameter it is quite possible to blow the second hole without troubling to stop up the first.

The writer has found that, with a little practice, a constant-level tube can be produced in 5 to 10 minutes but that, in some cases, subsequent adjustments of hole sizes have to be made before the level works properly.

# ROOT PENETRATION AND MOISTURE EXTRACTION IN SALINE SOIL BY CROP PLANTS<sup>1</sup>

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*U. S. Department of Agriculture*

Received for publication November 6, 1948

It is well known that different species of crop plants vary markedly in their adaptability to saline soil. The ability of a plant to thrive in the presence of soil salinity is conditioned by the degree of root penetration and the extent to which water and nutrients may be removed from the soil without absorbing toxic quantities of the ions present. The presence of salts in the soil moisture affects the roots of plants in two ways: first, the increased osmotic pressure of the soil solution restricts water entry (3); and second, certain of the ions present exert a specific toxic action on the activity of the plant cells (2, 7).

Many qualitative observations have been made on the relative salt tolerance of different species of plants, but quantitative data on this point are still meager. This study was undertaken to develop a method of quantitatively evaluating the tolerance of plants to saline soil. It was considered desirable to ascertain the comparative ability of the roots of different crop plants to penetrate a soil of specified salt content and their capacity to remove moisture.

## METHODS

Soil containers made of marine plywood coated with asphalt paint were used. They were 1 foot square and 3 feet deep on the inside. One side was attached with thumbscrews to permit easy removal for close examination of the soil column. The soil column was divided into six equal layers varying as to salt content as follows: top layer, no added NaCl; second layer, 0.05 per cent added NaCl; third, 0.1 per cent; fourth, 0.15 per cent; fifth, 0.2 per cent; and sixth, 0.25 per cent. Each layer of soil was added in four separate increments. Immediately upon the addition of an increment (about a 1½-inch layer of air-dry soil), sufficient water was sprinkled on to bring the average moisture content to 18 per cent, the value for the "normal moisture-holding capacity" (6) of the sample of Fallbrook loam used in this study. It was essential to keep water movement to a minimum in order to avoid movement of salt, and this amount of water was sufficient to moisten all the soil in the added increment without inducing appreciable gravitational movement of water.

Each addition of water contained sufficient NaCl to bring a designated increment of soil to the desired salt content. By adding the salt to the dry soil

<sup>1</sup> Contribution from the U. S. Regional Salinity Laboratory, Riverside, California, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, in cooperation with the eleven Western States and the Territory of Hawaii.

<sup>2</sup> Senior chemist, formerly associate physiologist, and formerly assistant agronomist, respectively.

by means of the water, it was felt that the distribution of salt would be more uniform than if the salt were first mixed with the increment of dry soil and then moistened.

In addition to the containers of saline soil, four were prepared in a similar manner except that no salt was added. With the moisture content at saturation, the untreated sample of Fallbrook loam had a pH of 7.6 and a specific conductance of 340 micromhos per centimeter at 25° C. The exchange complex was nearly saturated with calcium. The containers filled with this nonsaline soil were used to ascertain the degree of root penetration and moisture removal in the absence of induced salinity.

Red kidney beans, Mexican June corn, California Common alfalfa, and Shafter Acala cotton were selected as the crops to be grown. Seedlings of each crop were transplanted to three containers of salinized soil and to one of nonsaline soil on October 24, 1944. Single seedlings of corn and cotton and three seedlings of beans and alfalfa were planted in the containers.

The plants in each container were allowed to grow until they showed signs of marked moisture stress. At this time the removable side was taken from the container of soil, and the soil sampled at 12 successive levels—two levels within each of the originally distinct saline layers. At each level two 25–30-gm. samples were taken for soil moisture content and one 800-gm. sample for the determination of total solutes and chloride in the soil solution. The solutes in the soil moisture were determined in an extract obtained from the saturated soil placed on a Büchner funnel. The osmotic pressure of the soil solution at the moisture content of the soil at the time of sampling was calculated from the specific conductance of the soil extract as based on study of such relationship (1). The chloride content of the soil extract was determined by the method recommended by Reitemeier (4). The soil moisture tension of the various layers at the end of the experiment was evaluated from the soil moisture percentage data by means of a moisture sorption curve previously determined for this soil by using pressure-membrane and pressure-plate apparatus (5).

At the end of the tests, observations were made to determine the extent of root penetration into the various soil layers.

#### EXPERIMENTAL OBSERVATIONS

The four species of plants differed markedly in the strength of their symptoms of moisture stress. The pronounced rolling of the leaves of corn and the wilting of the leaves of alfalfa were easily identifiable symptoms of moisture stress. Bean plants showed a gradual reaction to stress over a relatively long period; it was difficult, therefore, to determine when a given degree of moisture stress was reached in the soil. The difficulty was increased in plants grown on saline soil. The cotton plants on the nonsaline soil wilted at a definite stage of moisture extraction, but no wilting occurred among the plants on the saline soil cultures. In this case some of the lower leaves of cotton abscised and plant growth stopped, but even though these plants were grown for some 2 months after the controls were harvested, the remaining attached leaves showed no loss of turgidity.

The permanent wilting percentage of the soil as determined by sunflower plants was 6.1. When the plants in the control cultures (nonsaline soil) showed moisture stress, it was found that the corn, alfalfa, and cotton had removed water rather uniformly from all layers, down to and including the 3-foot depth, to a value of 5.3 per cent. Beans removed the water in all layers down to a value of 6.5 per cent or less. These data show that the roots of all four species thoroughly permeated the lower strata of soil in these containers and that root penetration was not a limiting factor under nonsaline conditions.

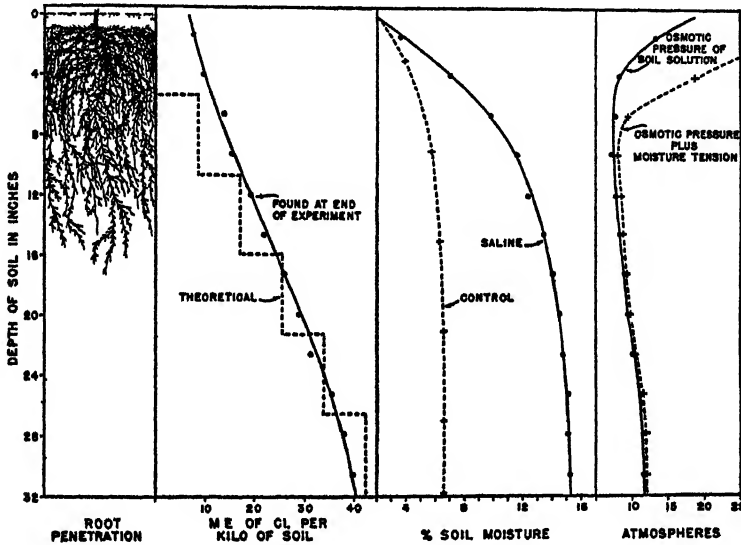


FIG. 1. PENETRATION OF SALINE SOIL BY ROOTS OF BEAN, MOISTURE AND SOLUBLE CHLORIDE CONTENTS OF SOIL, AND MOISTURE STRESS AT DIFFERENT LEVELS

Root distributions indicated by a diagrammatic composite of three replicates. Data for saline soils, averages of three replicates.

### Beans

The average dry weight of the tops of the bean plants on saline cultures was 7.2 gm. as compared with 29.0 gm. produced by the control culture. Figure 1 presents the average of the observations for the three containers of saline soil on which beans were grown. The agreement among the replicates for the soil moisture and soluble Cl content at a given level was rather good. The pooled standard error for the soil moisture percentages was  $\pm 0.26$ , and that for the chloride was  $\pm 1.05$  m.e. Cl per kilo of soil. The specific conductance of the saturated soil extract, from which the values for osmotic pressure were calculated, varied from 3.8 to 14.0 millimhos per centimeter at 25° C. with a pooled standard error of  $\pm 0.24$ .

Few bean roots penetrated the layer containing 0.1 per cent NaCl; virtually

none were found in the stratum to which 0.15 per cent salt was added; and none were found in the layers containing 0.2 and 0.25 per cent NaCl.

It is evident from the chloride determinations that there had been appreciable movement of salt in this soil, and that the movement was upward. Surface evaporation and water absorption by the roots were undoubtedly contributing factors.

The presence of salt in the soil had markedly reduced the absorption of water by bean roots. The moisture content of the lower layers of soil was somewhat below the level to which it was originally adjusted. This does not imply removal by the roots at these lower layers, as the observed movement upward of chloride could not have taken place without corresponding moisture movement.

The significance of the inability of bean roots to absorb soil moisture beyond a certain limit in saline soil which they had penetrated is enhanced by the uniformity of the observations on the calculated osmotic pressure of the soil solution and the summation of this osmotic pressure with the moisture tension—"total moisture stress" (8)—among the different layers. Evaporation from the surface of the container was undoubtedly the major contributing factor in the deviation of these curves from the general trend near the surface. Below this level and in the layers in which the roots had penetrated, the limiting "total soil-moisture stress" was found to be 8 to 9 atmospheres, of which osmotic pressure contributed 7 to 8 atmospheres.

### *Corn*

The tops of the corn plants on the saline culture averaged 16.9 gm. in dry matter per culture, in contrast with the control culture which produced 51.9 gm.

The results observed with the corn plants in saline soil are shown in figure 2. Within the observed data, the pooled standard error for these soil moisture percentages was  $\pm 0.56$  and that for the chloride content was  $\pm 3.87$  m.e. per kilo of soil. Thus the variability between replicates of corn was appreciably higher than that observed for beans. In this case the specific conductance of the extracts of the saturated soil varied from 2.63 to 13.5 millimhos per centimeter at 25° C. with a pooled standard error of  $\pm 0.41$ .

Only a few corn roots penetrated the layer containing 0.2 per cent salt, and none were found where 0.25 per cent NaCl was added. Compared with bean roots, corn roots appear to be able to penetrate a more saline soil.

The residual moisture content of the soil varied directly with the distribution of chloride, indicating that the moisture removal by the plant was inversely related to salt distribution. Because of the close relationship between salt distribution and residual moisture, the calculated osmotic pressure of the residual soil solution was found to be very uniform down through the various layers differing in percentage of salt. This critical osmotic pressure was found to be 10.5 to 11.5 atmospheres for the corn plants—appreciably higher than the value

observed with the beans. Here again, surface evaporation from the containers of soil caused a marked increase in the moisture tension of the soil near the surface.

### *Alfalfa*

The saline cultures produced an average of only 5.1 gm. dry weight of alfalfa tops as compared with 9.4 gm. for the control culture. The data for the cultures which grew alfalfa are shown in figure 3. For these data the standard error for the moisture percentages was  $\pm 0.11$  and that for the chloride content was  $\pm 1.98$  m.e. per kilo of soil. The extracts of the saturated soil had con-

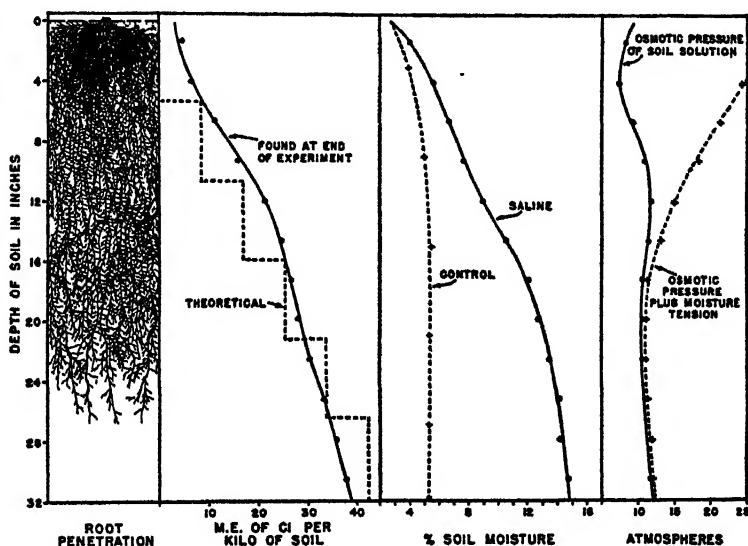


FIG. 2. PENETRATION OF SALINE SOIL BY ROOTS OF CORN, MOISTURE AND SOLUBLE CHLORIDE CONTENTS OF SOIL, AND MOISTURE STRESS AT DIFFERENT LEVELS

Root distribution indicated by a diagrammatic composite of three replicates. Data for saline soils, averages of three replicates.

ductances varying from 3.81 to 12.4 millimhos per centimeter at 25° C. with a pooled error of  $\pm 0.21$ .

Alfalfa roots penetrated the most saline layer in these boxes. On this basis, alfalfa may be regarded as more salt-tolerant than corn.

As noted with the corn plants, there was a remarkably close relationship between residual moisture content and the distribution of salt in the various layers of soil. This again resulted in a rather remarkable uniformity of the calculated osmotic pressure of the residual soil solution down through the strata of soil varying in percentage of salt. This osmotic pressure was found to be 12 to 13 atmospheres—slightly higher than was observed with corn.



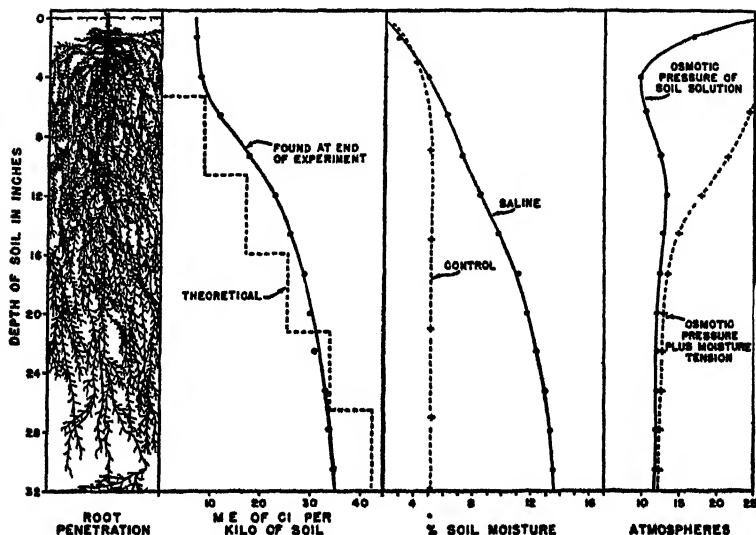


FIG. 3. PENETRATION OF SALINE SOIL BY ROOTS OF ALFALFA, MOISTURE AND SOLUBLE CHLORIDE CONTENTS OF SOIL, AND MOISTURE STRESS AT DIFFERENT LEVELS

Root distribution indicated by a diagrammatic composite of three replicates. Data for saline soils, averages of three replicates.

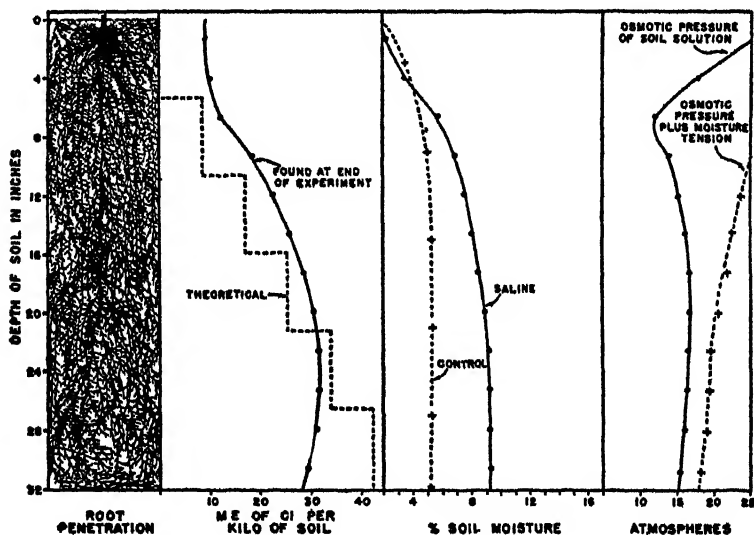


FIG. 4. PENETRATION OF SALINE SOIL BY ROOTS OF COTTON, MOISTURE AND SOLUBLE CHLORIDE CONTENTS OF SOIL, AND MOISTURE STRESS AT DIFFERENT LEVELS

Root distribution indicated by a diagrammatic composite of three replicates. Data for saline soils, averages of three replicates.

*Cotton*

The cotton plants on the saline cultures contained only 7.5 gm. of dry matter in their tops at the end of the experiment, whereas the control culture produced 20.9 gm. The results with cotton are shown in figure 4. The variability between replicates for the trend in moisture percentage was indicated by a standard error of  $\pm 0.31$ . The standard error for the chloride determination was  $\pm 2.32$  m.e. per kilo of soil. The variation in the specific conductances of the extract of the saturated soil was from 4.99 to 11.2 millimhos per centimeter at 25° C. with a standard error of  $\pm 0.31$ .

The cotton plants were carried for 6 weeks longer than any of the other species, yet the plants did not wilt. They made very little growth, many of the older leaves abscised, but no marked deficiency in turgescence of the leaves was observed. Because of the longer time involved, there was considerably more movement of the salt to the surface as a result of moisture evaporation at the surface. Nevertheless, a close correlation was found between salt distribution and residual moisture content of the soil. It is to be noted that the latter values were considerably lower in the more saline layers than was observed for the other species. This was probably related to the fact that the cotton roots penetrated in abundance the most saline strata.

Because of the larger quantity of moisture removed by the cotton roots, the residual osmotic pressure of the soil solution—16 to 17 atmospheres—was considerably higher than those observed for the other species of plants. Even the soil in the more saline portions, however, had dried sufficiently to develop appreciable moisture tension. The total stress on the root system, below the layers where surface evaporation was effective, was, therefore, 18 to 20 atmospheres.

## DISCUSSION

The relative salt tolerance of these four species of plants is the same as that usually observed in the field, that is, bean, corn, alfalfa, cotton in order of increasing tolerance. Whereas field observations are of a qualitative nature, the present study approaches a quantitative basis for evaluating the relative tolerance of plants to saline soil. Thus the plants may be segregated with similar results according to two criteria: first, the salt content limiting root penetration when the soil moisture percentage is near field capacity; and, second, the residual osmotic pressure of the soil solution when the plants show marked symptoms of moisture stress.

It must be conceded that the determination as to when the plants were showing a definite degree of moisture stress is somewhat arbitrary. Naturally, not all the cultures of plants of a given species reached this condition at the same time. With certain species (corn) there was as much as 2 weeks' difference between the first and the last inspection of the different cultures of a given crop; that is, the plants were harvested on reaching a specified condition of growth, and the reported values for error indicate the variation between different cultures of a given species as related to an arbitrarily selected condition of the plant.

This study has emphasized the importance of available water with respect to the salt tolerance of plants under field conditions. It is indicated that the supply of water available to the plant in the nonsaline or only slightly saline part of the root zone is the main limiting factor to plant growth so far as salinity is concerned. Thus, one could obtain a sample of soil from the root zone of a plant and find it moderately saline, yet the amount of salt in the sample might be entirely irrelevant to the growth response of the plant if another part of the root zone was nonsaline soil. Such a situation as this is very likely to exist under furrow irrigation of row crops. The soil under the furrow becomes leached and non-saline, whereas the salts accumulate in the row.<sup>3</sup> This indicates that certain very high values for the salt content of soils in which plants have been reported to be growing may be ascribed to faulty sampling.

#### SUMMARY

Bean, corn, alfalfa, and cotton plants were grown in containers, 1 foot square and 36 inches deep, of soil varying in added salt content with depth from none at the surface of 0.25 per cent at the bottom. Observations on these soil columns when the plants of each species were beginning to show marked moisture stress were as follows: Few bean roots penetrated the layer containing 0.1 per cent NaCl, and virtually none were found in the stratum containing 0.15 per cent salt. Only a few corn roots penetrated soil containing 0.2 per cent NaCl, and none were found in the presence of 0.25 per cent. A few alfalfa roots penetrated the stratum with 0.25 per cent salt. Cotton roots were present in abundance through all layers even the one containing 0.25 per cent NaCl. As the salt content of the soil strata increased, the roots of the various species showed a corresponding decrease in their ability to remove water. Water was removed from each layer to such a degree that final osmotic pressures of all layers in the soil column were nearly uniform. These critical osmotic pressures of the soil solution were found to be 7 to 8 atmospheres for beans; 10.5 to 11.5 atmospheres for corn; 12 to 13 atmospheres for alfalfa; and 16 to 17 atmospheres for cotton.

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# COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF POTASSIUM BY THE CHLOROPLATINATE METHOD<sup>1</sup>

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The determination of small amounts of potassium in soil extracts is a difficult problem. Recently, colorimetric methods have been stressed, particular attention being directed toward the cobaltinitrite method. Because of the variability of the composition of sodium-potassium-cobaltinitrite (8), this method is probably inferior to the older separation of potassium as the chloroplatinate salt and the subsequent conversion of the latter to the iodoplatinate, which can be measured colorimetrically. Although the reagents are more expensive, recovery of both platinum and iodine is easy. Consideration of economy is therefore not a good reason for not using the better method. As with most methods for potassium separation, ammonium and the rare alkali metals, rubidium and caesium, are included. Although the ammonium is easily removed, the two metals are unlikely to be quantitatively important in soil extracts, and could be determined separately for correction.

Morrell (7) in 1880 proposed the use of iodoplatinate for the colorimetric determination of potassium. Yoe (15, pp. 357-364) reported on the method of Cameron and Failyer (2). Shohl and Bennett (12) reported that 0.1 mgm. of potassium can be determined within 4 per cent when a color comparator is used. Tenery and Anderson (14) described a method for the determination of potassium in biological materials. St. John and Midgley (9) described a gravimetric procedure for the determination of potassium by the chloroplatinate method. None of these methods, when tested by the authors, possessed the desired sensitivity. The following work was undertaken, therefore, to extend the range of the chloroplatinate method to quantities as small as 0.01 mgm. of potassium.

The lack of desired sensitivity of previous methods was attributed, first, to washing of the precipitate by filtration, a procedure which necessitates the transfer of a small quantity of salts to a filter pad; and, second, to the use of sulfuric acid and heat to drive off ammonia. In the method here reported, the procedure was designed to permit the carrying out of the following operations without removal of the salt from the tube in which the potassium-containing ali-

<sup>1</sup> This paper reports part of the work done under Bankhead-Jones Project #29 at the Ohio Agricultural Experiment Station. This report and others appearing elsewhere are based on a thesis submitted by the senior author to the graduate faculty of the Ohio State University, Columbus, Ohio, in partial fulfillment of the requirements for the degree of doctor of philosophy.

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quot is placed: removal of ammonia (by oxidation with aqua regia), crystallization and washing of the precipitate, and development of the color. Washing of the precipitate is by centrifugation, the salts being firmly held in place by addition of a suspension of talc. A Wilkens Anderson KWSZ filter photometer was used to measure the color intensities, the depth of the absorbing solution being 20 mm.

Figure 1 shows the absorption curve of the iodoplatinate solution and the transmission curve of the Corning 440 filter. The iodoplatinate solution has a sharp maximum absorption at 490  $m\mu$  as reported by other workers.

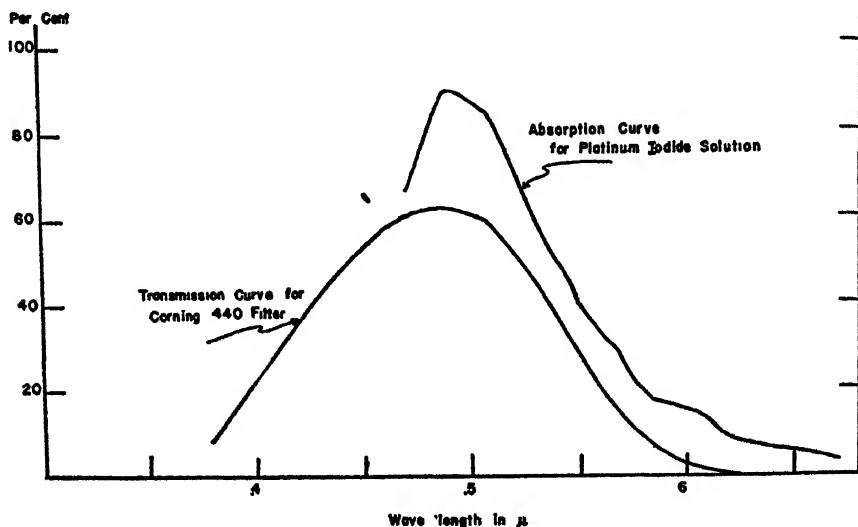


FIG. 1. ABSORPTION CURVE OF IODOPLATINATE SOLUTION AND TRANSMISSION CURVE OF THE CORNING 440 FILTER

The absorption curve was obtained on a Bausch and Lomb visual spectrophotometer, constant deviation type. The transmission curve was redrawn from "Glass Color Filters Manufactured by Corning Glass Works," page five.

#### EXPERIMENTAL

When the method described by Yoe (15) was modified by using centrifugation and oxidation of ammonia by aqua regia, unexpectedly large errors resulted. A study of the effect of pH value and potassium iodide concentration on the maximum color intensity revealed that pH value especially must be controlled.

Morrell (7) reported that an excess of iodide had no effect on color intensity but advised the use of a constant quantity of potassium iodide. He also found that the presence of hydrochloric acid intensified the color, "but always in proportion to the platinic salt present." Yoe (15) advised the addition of one drop of concentrated hydrochloric acid and 1 ml. of potassium iodide solution (containing 86 gm. per liter) to the chloroplatinate solution. Shohl and Bennett

(12) specified more accurately the amount of hydrochloric acid and potassium iodide to be added to develop the iodoplatinate color (5 ml. of 2 *N* potassium iodide and 1 ml. of *N* hydrochloric acid to 25 ml. of the potassium chloroplatinate solution). They reported that the rate of color development is proportional to the potassium iodide concentration and that heat and acid also hasten color development. Tenery and Anderson (14) developed the iodoplatinate color at 68° C. for 10 minutes and found that the photometer reading varied somewhat with the temperature of the solution at the time of reading. Adams and St. John (1) developed the color in 2 *N* potassium iodide solution and found appreciable deviations from the Beer-Lambert law. The deviations disappeared in the course of several days.

In our experiments, 0.50-ml. samples of a stock solution of chloroplatinic acid (0.325 gm. platinum per liter) were transferred directly to 50.0-ml. volu-

TABLE 1

*Percentage transmission of iodoplatinate solution as a function of pH values*  
pH 2.1 to 6.5, citric acid-sodium borate buffers; 0.163 mgm. platinum per 50.0 ml.

pH VALUE	TRANSMISSION
	<i>per cent</i>
2.1	68.0
2.5	74.5
4.1	89.5
4.6	90.0
5.2	95.5
6.5	96.5

metric flasks by means of a microburet. About 40 ml. of the buffer solution (indicated in tables 1 and 2) and the indicated amount of potassium iodide in solution were added. The volume was made to 50.0 ml. with the same indicated buffer solution. The final percentage transmission was read from 4 to 24 hours after the addition of the potassium iodide solution (12, 15). The citric acid-sodium borate buffers were prepared by titrating 0.25 *N* citric acid with 0.26 *N* sodium borate to give the desired pH values. The hydrochloric acid-potassium chloride buffers were prepared according to Lange's description (6, p. 943). A Leeds and Northrup thermionic potentiometer was used with a glass electrode to determine the pH values.

Of the considerable quantity of data collected during the development of the method, only a minimum is here reported. Table 1 illustrates the percentage transmission as a function of pH values in the region from pH 2.1 to 6.5 (citric acid-sodium borate buffers). The concentration of potassium iodide was maintained at 86 mgm. per 50 ml. As the pH value increases, the percentage transmission increases until no perceptible color remains. It is evident that no part of this pH range using these buffers is suitable for colorimetric determination of the iodoplatinate concentration.



Variation of pH value from 0.7 to 2.0 (hydrochloric acid-potassium chloride buffers) has no significant effect on final color intensity (table 2). Further work was therefore confined to this range.

The concentration of potassium iodide chosen (115 mgm. potassium iodide per 50 ml.) is higher than that recommended by Yoe (86 mgm.) but considerably lower than that recommended by Shohl and Bennett (1660 mgm. per 25 ml.). Concentrations higher than that chosen had no observed effect on the maximum color intensity, whereas lower concentrations resulted in less well poised redox

TABLE 2

*Percentage transmission of iodoplatinate solution as a function of pH values*  
pH 0.7 to 2.0, potassium chloride-hydrochloric acid buffers; 0.163 mgm. platinum per 50.0 ml.

pH VALUE	TRANSMISSION
	<i>per cent</i>
0.7	55.5
1.0	56.5
2.0	56.5

TABLE 3

*Color intensity and stability of iodoplatinate as functions of concentration of potassium iodide*

KI CONCENTRATION	TRANSMISSION OF IODOPLATINATE SOLUTION OF VARIOUS Pt CONTENTS*				
	65 $\gamma$ Pt	163 $\gamma$ Pt	489 $\gamma$ Pt	815 $\gamma$ Pt	1630 $\gamma$ Pt
<i>mgm.*</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
23	79.1	58.1	25.3	ppt.	ppt.
69	77.8	57.6	25.1	ppt.	ppt.
115	78.8	56.6	25.3	14.5	6.6
230	....	57.2	....	....	....
460	....	55.8	....	....	....

\* Per 50 ml. solution.

systems with respect to pH value changes. When 69 mgm. potassium iodide or less was added to 50 ml. of chloroplatinate solution containing 0.815 mgm. platinum (equivalent to 0.325 mgm. potassium), metallic platinum was precipitated (see table 3).

Temperature variations of the solution from 15° C. to 38° C. during color development had no effect on the maximum color attained. The use of heat to increase the rate of color development is a questionable procedure, since boiling will destroy the color.

Studies on the rate of color development showed that color intensity reached a maximum in less than 2 hours when the foregoing conditions obtained. After 24 hours, sufficient iodine was usually liberated, by the action of oxygen on hydriotic acid, to affect color intensity. Increases of the potassium iodide and

hydrogen-ion concentrations decreased the time interval before which liberation of iodine affected color intensity (see table 4).

PROCEDURE

The method finally adopted is as follows: Evaporate the neutral, normal ammonium acetate soil leachate to dryness, add 10 ml. of aqua regia, cover, and heat to dryness. Repeat the aqua regia digestion. Add 5 to 10 ml. of 60 per cent perchloric acid and fume off the excess on a gas plate. Add about 0.5 ml. of concentrated sulfuric acid and repeat the fuming to convert the salts to sulfates. Dissolve the residue in hot, dilute hydrochloric acid and make up to volume. Pipette aliquots of the ammonia-free and organic-matter-free

TABLE 4

*Effect of pH value and potassium iodide concentration on separation of iodine in hydrochloric acid-potassium chloride buffer solutions*

pH	IODINE SEPARATION FROM SOLUTION OF DIFFERENT KI CONCENTRATIONS	
	115 mgm. KI*	230 mgm. KI*
0.7	+†	+
1.0	+	+
1.2	+	+
1.4	+	+
1.6	—	+
1.8	—	+
2.0	—	—

\* Per 50 ml. solution.

† The plus sign indicates that the yellow color of free iodine was observed 24 hours after addition of potassium iodide. At 4 hours no color was visible except in the pH 0.7 buffer. At 48 hours all solutions had a marked yellow tint.

solution, preferably containing about 0.1 mgm. potassium, into 50- ml. round-bottom centrifuge tubes and evaporate to dryness on a high-pressure steam plate, the tubes being held in a concrete block or transit box to hasten evaporation by heating the full length of the tube. Add one to five drops of concentrated hydrochloric acid (depending on the amount of calcium sulfate present), 0.5 ml. of 1 per cent chloroplatinic acid (theoretically sufficient to precipitate 750  $\mu$  of potassium), and about 1 ml. of distilled water to each tube. Mix and evaporate to dryness on a steam plate, avoiding prolonged heating after dryness is attained. Cool the tubes to room temperature and add 1 ml. of a 2 per cent suspension of talc (previously extracted with hydrochloric acid and then washed free of chlorides) in 80 per cent alcohol. Wash the potassium chloroplatinate crystals and talc free of other chloroplatinates by centrifugation, using 10 ml. of 80 per cent ethyl alcohol saturated with potassium chloroplatinate as the wash liquid. Repeat this process three times. Drain the tubes by inversion over a paper towel and dry off the remaining alcohol by passing a current of air through the tubes for a few minutes by means of an aeration manifold.

Add 10 ml. of buffer solution (29.8 gm. of potassium chloride plus 32 ml. of concentrated hydrochloric acid in 9570 ml. of distilled water, pH 1.5) to each tube and 1 ml. of potassium iodide solution (11.5 gm. per 100 ml. of solution). Allow the color to develop for at least 2 hours at room temperature, then filter the solution under suction on a filtration manifold. Dilute the filtrate to 50 ml. with the buffer solution and read in a photometer, using a Corning 440 filter and an absorption cell 20 mm. deep, not later than 24 hours after the addition of the potassium iodide. If a spectrophotometer is used, set the wave length at 490  $m\mu$ . The milligrams of potassium can be read either from an analytical curve or a table previously prepared from standard potassium chloride solutions.

#### ACCURACY

When the foregoing conditions were maintained, determinations of eight samples of 0.066 mgm. potassium from its chloroplatinate salt yielded a mean

TABLE 5  
*Accuracy and range of method*

POTASSIUM ADDED	POTASSIUM RECOVERED*	TRANSMISSION*
$\gamma$	$\gamma$	per cent
10.0	10.0 $\pm$ 1.3	88.4 $\pm$ 0.7
30.0	30.0 $\pm$ 1.2	74.5 $\pm$ 0.7
50.0	50.0 $\pm$ 3.4	64.0 $\pm$ 1.9
80.0	80.0 $\pm$ 2.5	50.3 $\pm$ 0.7
150	150 $\pm$ 2	33.1 $\pm$ 0.3
200	200 $\pm$ 4	25.4 $\pm$ 0.4
250	250 $\pm$ 2	20.6 $\pm$ 0.2
350	350 $\pm$ 3	13.9 $\pm$ 0.2
500	500 $\pm$ 7	9.4 $\pm$ 0.1

\* The error is expressed as the maximum variation from the mean of triplicates.

error of less than  $\pm 1.5$  per cent. Extracts of seven samples of a well-mixed lot of soil, each containing 0.134 mgm. potassium, were analyzed in duplicate (14 determinations). The average variation from the mean was  $\pm 1.2$  per cent, with a maximum variation of 3.7 per cent. On the basis of 11 samples of soil extracts containing from 0.104 to 0.231 mgm. potassium, each sample analyzed either in triplicate or quadruplicate (a total of 38 determinations), the standard deviation of percentage variations from the mean<sup>3</sup> was 1.7 per cent. The maximum variation was 4.3 per cent from the mean.

$$\sigma = \sqrt{\frac{\sum \left[ \frac{100(x - \bar{x})}{\bar{x}} \right]^2}{N - 1}}$$

where  $\sigma$  = standard deviation of the percentage variations from the mean,  $\bar{x}$  = mean of each set of determinations,  $x_1$  = value of each determination, and  $N$  = the number of determinations.

Table 5 indicates the accuracy and range of the method. Potassium was determined in triplicate from known potassium chloride concentrations over the range 0.010 to 0.500 mgm. potassium.

For percentage transmissions of less than 25.4 (corresponding to 0.200 mgm. potassium) the indication is that the instrument used may be read more accurately than  $\pm 0.5$  scale divisions, since the error in the determination of potassium is less than an assumed error based on that variation in transmission reading (table 6). In the range less than 0.200 mgm. potassium, the error in the method for the determination of potassium approximates the assumed error in transmission reading.

TABLE 6

*Comparison of error in potassium determination with error in transmission measurement*  
Error in transmission measurement based on assumed  $\pm 0.5$  scale division variation\*

POTASSIUM ADDED	ERROR IN POTASSIUM DETERMINATION	
	Based on recovery of potassium	Based on assumed variation in transmission measurement
$\gamma$	<i>per cent</i>	<i>per cent</i>
10.0	13.0	10.0
30.0	4.0	3.0
50.0	7.0	2.0
80.0	3.1	1.3
150	1.3	1.6
200	2.0	2.0
250	0.8	2.4
350	0.9	2.9
500	1.4	6.0

\* The instrument was divided into 100 major scale divisions and could be read to the nearest 0.1 scale division.

#### DISCUSSION

Organic matter must be destroyed, since the presence of protein will cause a low recovery of potassium (12). If the sample had been digested with perchloric acid, it was found necessary to convert the perchlorates to sulfates, since the presence of the former salts interfered with the recovery of potassium, probably by the formation of insoluble potassium perchlorate. St. John and Midgley (9) used perchloric acid digestion without conversion to sulfates and experienced no such difficulties. It is improbable that the heat treatment they used ( $350^{\circ}\text{C}$ . for 15 to 30 minutes in a muffle furnace) was sufficient to decompose the perchlorates; but it is possible that their use of a much greater excess of chloroplatinic acid may have overcome the interference of the perchlorate ion. Hydrogen peroxide used as a digesting reagent was also found to interfere, probably by the oxidation of potassium chloride to potassium perchlorate.

Ammonia, of course, must be removed before the precipitation of the potassium as the chloroplatinate. Ammonium salts and other nitrogen compounds are de-

composed with aqua regia and driven off as free nitrogen, nitrosyl chloride, etc. (11). Experiments showed that one treatment as specified was usually sufficient, and no ammonium ions survived a repetition, as evidenced by the Nessler test. This method of removing ammonia is effective and is safer and more rapid than volatilization of ammonium sulfate by heat.

Prolonged heating of the crystallized chloroplatinates, which would result in dehydration of the sodium chloroplatinate, is to be avoided because the dehydrated salt is less soluble in alcohol than is the hydrated salt (4, p. 519). Because sodium chloroplatinate is more soluble in 80 per cent alcohol than in 95 per cent alcohol, the former is used (3). Saturation of the 80 per cent alcohol with potassium chloroplatinate prevents loss of potassium chloroplatinate during washing, as the potassium salt is appreciably soluble in 80 per cent alcohol (5, p. 391).

Washing the potassium chloroplatinate crystals by centrifugation is more rapid than washing by filtration and eliminates a potential source of error, as the minute quantity of crystals is not removed from the tube in which crystallization occurs, until after the salts are in solution and the color is developed.

Until a means was devised to retain the potassium chloroplatinate crystals at the bottom of the centrifuge tube, difficulty was experienced in decanting the supernatant liquid without disturbing the crystals. Of many materials tried, talc was found to be best suited for the purpose. During centrifugation it forms a compact pad on top of the crystals. Residual alcohol, after washing, was completely evaporated because alcohol interferes with color development (15). The alcohol was evaporated by an air current because, when heated, it may cause precipitation of metallic platinum from its salt.

The analytical curve of the iodoplatinate solution as prepared under the conditions specified is nonlinear, although Schlesinger and Tapley (10) reported that iodoplatinate in aqueous solution obeys Beer's law. The use of a filter photometer in which the filter transmits light on both sides of the inflection point of the absorption curve probably accounts for the analytical curve's being nonlinear. According to States and Anderson (13), if a solution obeys Beer's law, analytical curves obtained by filter photometers are, in general, nonlinear.

#### SUMMARY

A colorimetric method for the determination of potassium in soil extracts by the chloroplatinate procedure, having a range from 0.010 to 0.500 mgm. potassium, is described. Simple measures for ensuring reproducible color intensities of iodoplatinate solutions are given.

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# THE WATER TABLE, EQUIPOTENTIALS AND STREAMLINES IN DRAINED LAND: V. THE MOVING WATER TABLE

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Attention has been drawn on occasion (1, 5) to the limitations of the method of electric analogues for the solution of problems of fluid flow; it has been said that the method can be used only for the state of the stationary water table. Though it is clear that no direct analogue of a rising or falling water table is practicable, the purpose of this paper is to show that a solution in such circumstances may be obtained indirectly by adaptation of the method.

Let us suppose that figure 1 is a cross section of permeable soil, with all conditions uniform in the direction perpendicular to the plane of the paper, so that we have a two-dimensional problem. The height  $h$  of any point is measured relative to the impermeable floor and the horizontal distance  $d$  is measured from some arbitrarily chosen vertical line. For the sake of simplicity of introduction, let us further suppose that the soil is one of very uniform pore-size, so that the capillary fringe is well defined (2) and has an upper boundary which separates a lower zone of saturated soil, of moisture content  $c_s$ , from an upper zone of unsaturated soil, of lower and sensibly uniform moisture content  $c_u$ . In fact, of course,  $c_u$  is not uniform, but at least its variations are negligible compared with the difference between  $c_s$  and  $c_u$ . In figure 1 the position of the fringe boundary at an initial instant of time is shown at  $P'Q'$  and, the rainfall rate  $a$  being assumed insufficient to maintain this position, the subsequent position after a time interval  $\delta t$  is lower, at  $P''Q''$ . In the time interval  $\delta t$  the moisture content in the zone  $P'Q'Q''P''$  is reduced from  $c_s$  to  $c_u$ , and the water released flows away below the boundary, since only below the boundary is the permeability appreciable. The falling water table thus introduces an additional downward flux across the boundary; if we consider a unit horizontal area at the point  $(d, h)$ , at which point the fall of the boundary is  $-\delta h_d$ , the volume of water,  $\delta Q_d$ , released across the boundary is given by

$$\delta Q_d = -(c_s - c_u)\delta h_d$$

where  $c_s$  and  $c_u$  are expressed as volumes of soil water per unit volume of soil. In the limit, when the time interval is infinitesimally small and the initial and final boundaries are indistinguishable from the mean position  $PQ$ , the total flux  $\psi_d$  per unit area is given by

$$\begin{aligned}\psi_d &= a - (dQ/dt)_d \\ &= a - (c_s - c_u)(dh/dt)_d\end{aligned}\tag{1}$$

The construction of electric analogues for a variety of steady states has already been described (1, 2, 3). The condition of uniform current input at the "boundary," analogous to uniform flux density when  $dh/dt$  is 0, must for present pur-



poses be replaced by a current distribution analogous to the flux distribution described by equation (1), in which  $dh/dt$  is not initially known but must itself be determined in the course of the solution. It may be remarked here that when the water table is rising, that is, when  $dh/dt$  is positive, the total flux is less than the rainfall rate by an amount equal to the rate of storage of ground water; this case presents difficulties which require further consideration, and will receive no general discussion here.

The process of solution may best be demonstrated by considering a particular problem. Let us consider the drainage system discussed in parts I to III (1, 2, 3), namely, drains of uniform diameter, depth, and spacing laid in land of uniform depth and permeability. As before, we need only investigate the conditions in a cross section bounded by a vertical plane through a drain line and another plane parallel with the first and midway between this drain line and its neighbor. The initial fringe boundary must be known together with the sub-

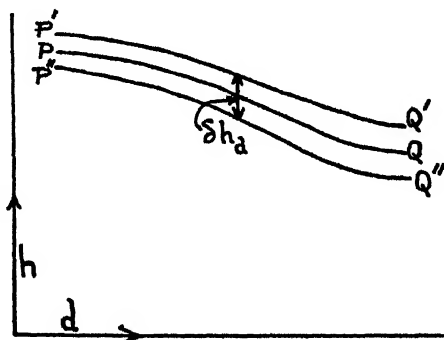


FIG. 1. CROSS SECTION OF A PERMEABLE SOIL WITH WELL-DEFINED CAPILLARY FRINGE, SHOWING FALL OF FRINGE BOUNDARY  $P'Q'$  WITH REDUCED RAINFALL

See text for full explanation of symbols

sequent rainfall rate. Let us therefore, as an example, trace the history of the fringe boundary and water table after the rainfall which had maintained these surfaces in their equilibrium positions suddenly ceases. In figure 2 we see the initial boundary  $PQ$  and a series of subsequent boundaries  $RS$ ,  $TU$ , and so on. It will also be necessary to refer to the intermediate positions  $pq$ ,  $rs$ ,  $tu$ ,  $vw$  bisecting the respective decrements.

The initial boundary is found in the usual way by fixing the point  $P$  arbitrarily in the analogue and, by trial and error, satisfying the two conditions that the boundary is the locus of points such that (3)

$$V = Ah - C \quad (2)$$

while the current input is uniformly distributed over that boundary. In equation (2),  $V$  is the electric potential,  $h$  is the height of the point considered, measured from the drain level as datum, and  $A$  and  $C$  are constants which are the analogues of the quantities  $g\rho$  and  $p_0$  in the equation

$$\phi = g\rho h - p_0 \quad (3)$$

which is appropriate to the fringe boundary in the soil. In equation (3)  $\phi$  is the hydraulic potential,  $g$  is the acceleration due to gravity,  $\rho$  is the density of water, and  $p_c$  is the critical pressure deficiency at which the moisture content changes from  $c_s$  to  $c_u$ . Since we are not attempting to make an analogue to represent a preselected soil, and since the choice of an electric potential to represent a given gravitational potential is only a matter of convenience, the constants  $A$  and  $C$  may be selected for convenience only, it being usual to select the fringe boundary height at  $P$  and the fringe thickness at the same point, adopting the values of  $A$  and  $C$  which emerge as a result (2).

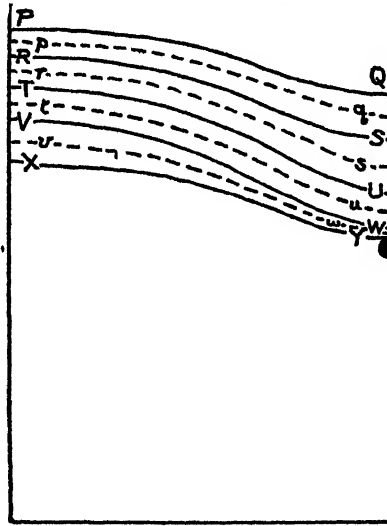


FIG. 2. SUCCESSIVE POSITIONS OF THE FRINGE BOUNDARY AFTER SUDDEN CESSATION OF RAINFALL FOLLOWING A STABLE WATER TABLE

See text for full explanation of symbols

For the next subsequent boundary position  $RS$ , the conditions are changed. The rainfall having ceased, the flux across the boundary,  $\psi$ , is, from (1)

$$\psi_d = -(c_s - c_u)(dh/dt)_d \quad (4)$$

Provided that the descent from  $PQ$  to  $RS$  is a short one in a brief time interval  $\delta t$ ,  $(dh/dt)_d$  along  $RS$  may be replaced without serious error by  $(\delta h/\delta t)_d$ , where  $-\delta h_d$  is the fall from  $PQ$  to  $RS$  at the distance  $d$  from the drain ordinate. Since  $\delta t$  is constant over the whole of  $RS$ , the flux  $\psi_d$  is proportional to  $\delta h_d$ , and consequently the current input  $i_d$  per unit length of "fringe boundary" in the analogue must be distributed so as to satisfy the relationship

$$i_d = K \delta h_d \quad (5)$$

where  $K$  is a constant. Equation (2) must also, of course, be satisfied, and since we still are dealing with the same soil and scale of representation as before, the

constants  $A$  and  $C$  must, it would seem, be retained. Assuming this to be so, we proceed by selecting the point  $R$ , which we are at liberty to do since we have not defined the time interval  $\delta t$ , and constructing  $RS$  to comply simultaneously with equations (2) and (5). The constant  $K$  is not open to free choice, since the total current input is determined jointly by the constant sheet conductivity of the analogue and the already defined constants  $A$  and  $C$ . The adjustment of  $RS$  having been made satisfactorily, the potential field is plotted, the water table found as the locus of points for which (3)

$$V = Ah \quad (6)$$

and the flow net is drawn, primarily in order to check the value of the sheet conductivity. One then proceeds in like manner to determine subsequent stages.

The relative time intervals elapsing between the various stages are determined as follows: Let  $i_1$  and  $i_2$  be the total current inputs at the end of stages 1 and 2 respectively, that is, over the boundaries  $RS$  and  $TU$  of the analogues. Let  $\Psi_1$  and  $\Psi_2$  be the total rate of flow of water across the boundary to which  $i_1$  and  $i_2$  are analogous. If  $(\delta t)_1$  and  $(\delta t)_2$  are the respective time intervals between  $PQ$  and  $RS$  and between  $RS$  and  $TU$ , while  $\Delta_1$  and  $\Delta_2$  are the respective cross-section areas between these pairs of curves, then

$$\begin{aligned} i_1/i_2 &= \Psi_1/\Psi_2 \\ &= (\Delta_1/\delta t_1)/(\Delta_2/\delta t_2) \end{aligned} \quad (7)$$

from which the ratio  $\delta t_1/\delta t_2$  can be calculated, all the other quantities being measured in the experiment. The absolute values of  $\delta t_1$  and  $\delta t_2$  can be arrived at only in the light of information as to the properties of the particular soil under discussion, and will be treated at a later stage. Though all the agriculturally important results can be expressed in one diagram, namely, a family of curves representing the height of the fringe boundary, at specified distances  $d$ , plotted against time, it is informative to plot also the succession of positions of the boundary, as in figure 2, in a second diagram. A similar pair of diagrams might also be presented for the water table succession.

If the adjustments of the analogues by trial and error had to be carried out exactly as described above, it would be a very tedious process. Fortunately the element of freedom may be extended. If we imagine an adjustment completed in the foregoing manner, and then the electric potentials at all points of the analogue were to be changed in the same proportion, as, for example, by a change of voltage of the battery supplying all the currents, then all the current elements would also be changed in the same proportion, the conductivity of the analogue remaining, of course, unchanged. Consequently equation (2) would still be satisfied, but with different constants  $A'$  and  $C'$ , the ratio  $A'/C'$  being the same as  $A/C$ ; and equation (5) would still be satisfied, but with a different constant,  $K'$ . Hence we should arrive at the same shapes of boundaries if we allow ourselves freedom at each stage in the choice of  $A$ ,  $C$ , and  $K$ , ensuring only that  $A/C$  is constant throughout the succession of stages. We can then

calculate by proportion the current input which would have been observed had  $A$  and  $C$  been held separately constant throughout, from which calculated current we can then obtain the various ratios between subsequent time intervals. Finally, it is possible with experience to forecast the boundary one stage ahead sufficiently well to estimate the descent from the medial position  $pq$  to  $rs$ ,  $rs$  to  $tu$ , and so on; the value of  $\delta h/\delta t$  is a better approximation to  $dh/dt$  along  $RS$  when  $\delta h$  refers to the interval  $pq$  to  $rs$  than when it refers to the interval  $PQ$  to  $RS$ , and similarly for the remaining intervals.

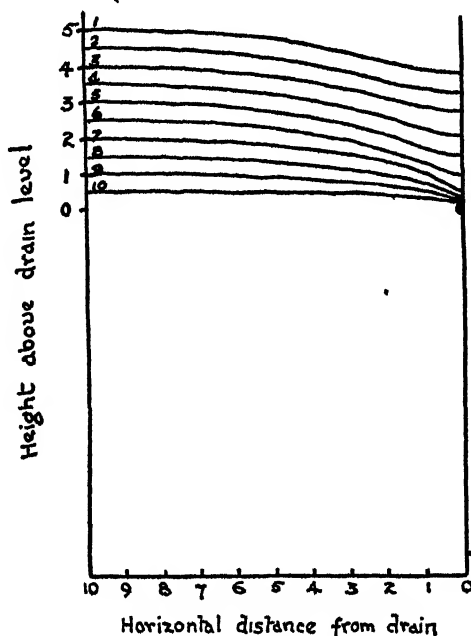


FIG. 3. SUCCESSION OF FALLING WATER TABLES, BEGINNING WITH THE STEADY STATE, AFTER RAINFALL CEASES

The numbers against the water tables are the order of succession. The horizontal and vertical distances indicated refer to the dimensions of the analogue, in centimeters, but may be interpreted on any scale.

#### EXPERIMENTAL RESULTS

In the first experiments, the results of which are shown in figures 3, 4, and 5, it is assumed for simplicity that the soil is one that does not support a capillary fringe; the boundary of the ground-water zone, therefore, is the water table. The relative dimensions of drain diameter, depth, and spacing and soil depth are sufficiently indicated in figure 3. The boundary conditions are identically those already discussed, namely, a complete cessation of rainfall following a stable water table.

The results of the second series of experiments are shown in figures 6 and 7. The only change from the first series is that the initial state is that of water-

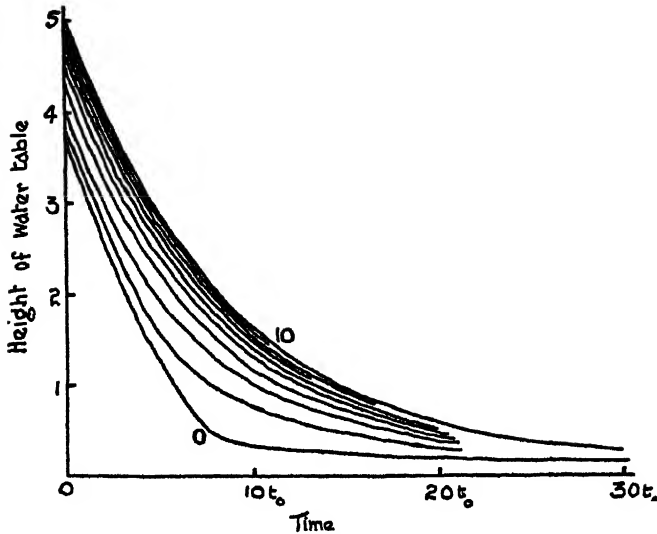


FIG. 4. VARIATION OF WATER-TABLE HEIGHT WITH TIME, AT VARIOUS HORIZONTAL DISTANCES FROM THE DRAIN, UNDER THE CONDITIONS OF FIGURE 3

The numbers 0 and 10 against the bounding curves refer to distance from the drain. The numbers 1, 2, etc. proper to the intermediate curves are omitted to avoid confusion. Curve 9 is also omitted, since it is hardly distinguishable from 10. The time unit  $t_0$  is arbitrary, and is taken throughout the paper as the time required for the water table to fall from half-way between stages 1 and 2 (fig. 3) to half-way between stages 2 and 3.

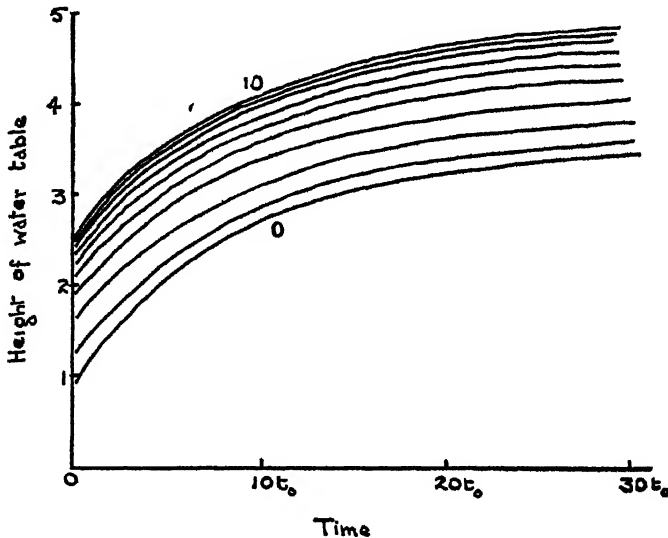


FIG. 5. THE SAME AS FIGURE 4, BUT FOR A RISING WATER TABLE, BEGINNING AT STAGE 6 OF FIGURE 3, WITH RAINFALL APPROPRIATE TO A FINAL STATE GIVEN BY STAGE 1 OF FIGURE 3

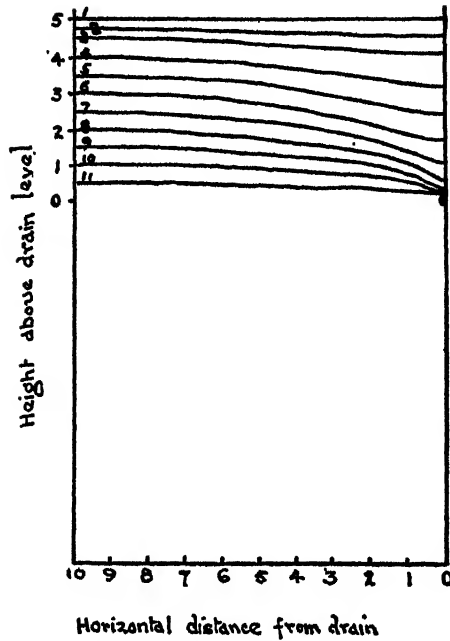


FIG. 6. THE SAME AS FIGURE 3, BUT WITH AN INITIAL STATE OF WATERLOGGING TO THE SOIL SURFACE (SURFACE WATER TABLE)

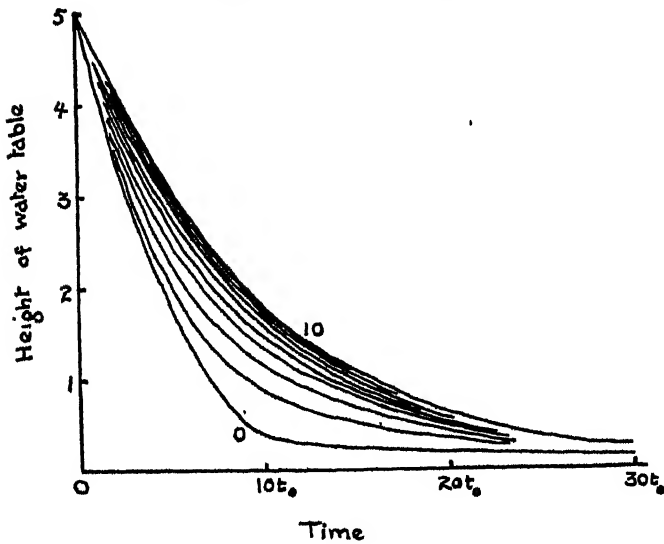


FIG. 7. THE SAME AS FIGURE 4, BUT FOR THE SAME INITIAL STATE (SURFACE WATER TABLE) AS FIGURE 6

logging to the surface instead of a stable water table defined by a particular rainfall rate.

In the third series of experiments, the soil considered was shallow, the drains resting on the impermeable floor, and the initial state was, as for the second series, complete flooding. The results are shown in figures 8 and 9.

Finally, the previous case was repeated, with the difference that a capillary

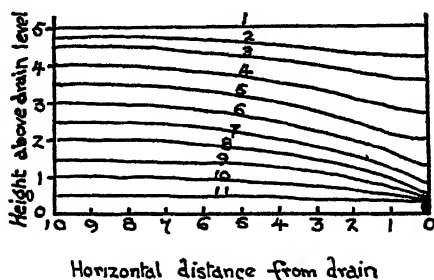


FIG. 8. SUCCESSION OF FALLING WATER TABLES IN SHALLOW SOIL, WITH DRAIN ON THE IMPERMEABLE BED, AND STARTING WITH AN INITIAL SURFACE WATER TABLE; ZERO RAINFALL

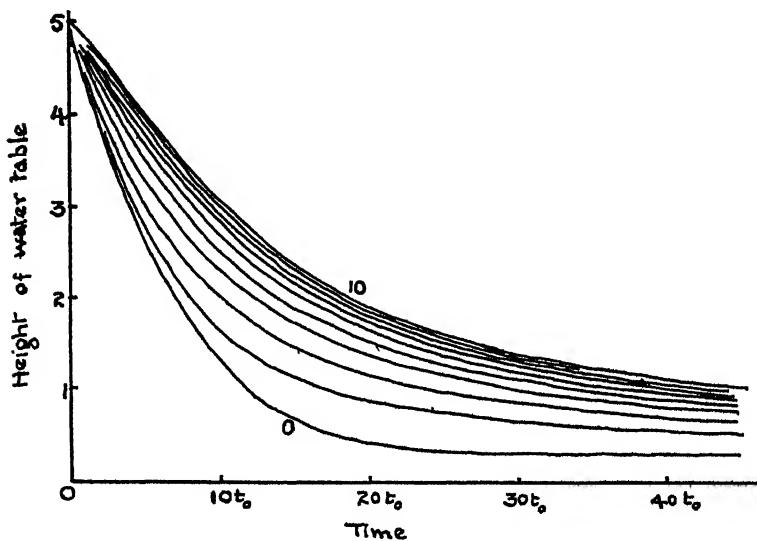


FIG. 9. VARIATION OF WATER-TABLE HEIGHT WITH TIME, AT VARIOUS HORIZONTAL DISTANCES FROM THE DRAIN, CORRESPONDING TO FIGURE 8

fringe was taken into account. The fringe thickness was arbitrarily chosen to be 1 cm. on the analogue at the midpoint between drains at the end of the first interval, the depth of the drains being 5 cm. and the semispacing 10 cm. throughout. The results are shown in figures 10 and 11. There is no capillary fringe at the initial instant, since surface flooding implies a surface water table. With cessation of rainfall and the removal of free water from the surface, the capillary

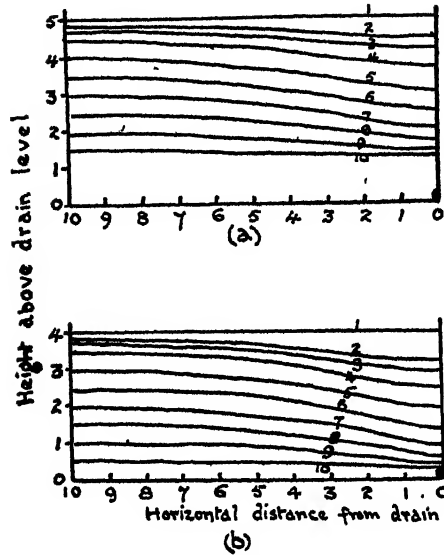


FIG. 10. (a) SUCCESSION OF FALLING CAPILLARY FRINGE BOUNDARIES, AND (b) SUCCESSION OF FALLING WATER TABLES, IN SHALLOW SOIL, AS IN FIGURE 8, WITH INITIAL SURFACE WATER TABLE, ZERO RAINFALL, AND AN INSTANTANEOUSLY FORMED CAPILLARY FRINGE INITIALLY OF UNIT THICKNESS (1 CM. ON THE ANALOGUE)

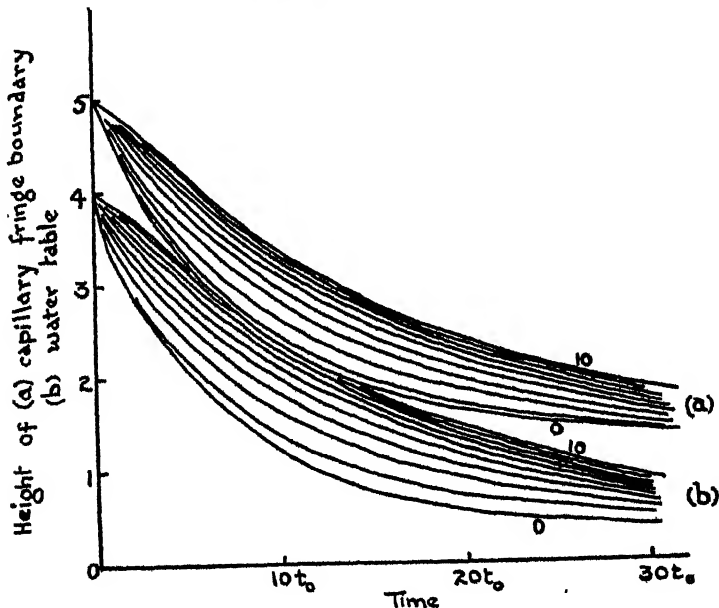


FIG. 11. (a) VARIATION OF HEIGHT OF FRINGE BOUNDARY, AND (b) VARIATION OF HEIGHT OF WATER TABLE, WITH TIME AT VARIOUS HORIZONTAL DISTANCES FROM THE DRAIN, CORRESPONDING TO FIGURE 10



fringe forms without loss of soil water, that is, without a contribution to the total flux, and therefore forms instantaneously.

#### DISCUSSION

The feature of figures 3 and 4 which first attracts attention is that the water table falls almost equally everywhere over the greater part of its descent, until, in fact, its height at the drain ordinate is very little above the level of the drain itself. At this stage the water table at the midpoint between drains is, of course, still fairly high, and since the final state of the horizontal water table at drain level must be reached by all points at the same time, it follows that the rate of fall must decrease very much more suddenly at the drain ordinate than at the midpoint. This course of events is shown in figure 4. The curves are all more or less parallel for the first stage of the descent. After this, curve 0 flattens out the most suddenly and completely, and curve 10 decreases in slope the most gradually.

The time scale of figure 4 is an arbitrary one, and the relative time intervals between stages in the descent of the water table hold true for the particular soil and drain cross section shown, no matter what the soil permeability or the scale on which the soil section may be interpreted. More precise discussion must be based upon the physical characteristics of a particular selected soil and the particular dimensions, depths, and spacings of the drains. As an example, we may choose a drain spacing of 10 m. Figure 3 interpreted on this scale gives a drain diameter of 15 cm. and an initial water-table height of 250 cm., relative to drain level, at the midpoint, the impermeable floor being 500 cm. beneath the drains. Since the capillary fringe has been assumed to be of negligible thickness, the soil must be a coarse sand at least, with large pores, and will therefore have a relatively high permeability. A medium consisting of sand particles 1 or 2 mm. in diameter would develop a capillary fringe of only about 5 cm. thickness, negligible in relation to the dimensions of the flow net, and would have a permeability of about  $10^{-4}$  c.g.s. units. Our problem is to determine the arbitrary unit  $t_0$  of figure 4, this being the time interval between the stages  $pq$  and  $rs$ , for which the mean stage is  $RS$ .

From the flow net for the initial steady state  $PQ$ , together with the aforementioned value of permeability of  $10^{-4}$  c.g.s. units, we can calculate that the total amount of water crossing the half-section of water table per second is 14.1 cc., if a flow thickness of 1 cm. is assumed. The flow nets are, in fact, not shown in this paper, since there are too many of them for convenient reproduction, but the method of calculating the permeability from rainfall rate and flow net, that is, the converse of the above calculation, has been described in part I (1). The total current input in the analogue at this stage, simulating this water input, was 286.5 units, the units being arbitrary but remaining constant throughout this discussion. The total current input in the analogue for the second stage,  $RS$ , after correction for possible changes in the resistance of the sheet conductor, and calculated to the same value of  $A$  as for  $PQ$ , was 261.0 units. This represents, by proportion, a total water-flow across the half-section

of water table of 12.8 cc. per second. This may be assumed to be the average flow rate while the water table falls from  $pq$  to  $rs$ , a decline which involves the unsaturation of 12,500 cc. of soil, when a thickness of 1 cm. of soil is assumed. If the assumed value of pore space emptied in this process [that is,  $c_s - c_u$  in equation (1)] is the reasonable figure of 35 per cent, then the fall of water table from  $pq$  to  $rs$  involves a release of 4,380 cc. of water in the time interval  $t_0$  seconds. Equating  $4,380/t_0$  to 12.8 cc. per second, we find that  $t_0 = 340$  seconds, or 0.0945 hours. Thus, in this case, the whole course of figure 4 is run in about 2.8 hours.

Though it is no part of this discussion to deal generally with the case of a rising water table, it may be remarked in passing that a considerable part of the water-table sequence shown in figure 3 may be interpreted in the reverse direction. The initial steady state and the subsequent five stages present, as has been noted, a sequence of water tables essentially of the same shape throughout the course of the descent, and each being uniformly displaced below the preceding stage. Hence the factor  $(dh/dt)_a$  of equation (4) is independent of the horizontal distance  $d$ , and the flux  $\psi_a$  is uniformly distributed; the analogues for these stages therefore have uniformly distributed electric current input. This condition in the analogue fits equally well a uniformly rising water table, since again the factor  $(dh/dt)_a$ , this time in equation (1), is independent of  $d$  but is now positive, while the rainfall term  $a$  is also uniformly distributed with respect to  $d$ , so that again  $\psi_a$  is uniformly distributed. Hence, provided that the rainfall fluctuations are such as to keep the water table within the region of stages 1 to 6 of figure 3, this water table will rise and fall as a whole without change of shape. The mean water table will also be identical with the steady-state water table for some mean value of rainfall intensity, since again the analogue condition for this mean steady rainfall is that of uniform current input. This conclusion was reached tentatively in part I of this series (1).

We can construct figure 5 for the rising water table, corresponding to figure 4 for the falling water table and starting with stage 6 of figure 3 as the initial stage. One may, of course, choose a rainfall rate freely; that chosen here is the rate which is just sufficient to bring the water table back ultimately to stage 1 of figure 3 as the steady state. In this figure,  $t_0$  is the same time interval as in figure 4 and may be interpreted for a particular case in just the same way as is shown above.

Little comment is called for in connection with figures 6 and 7. In the early stages of descent the fall of the water table is much more rapid immediately above the drainline than elsewhere, thus tending toward the production of a water table of the now familiar shape. At stage 7 in figure 6 the water table over the drain has caught up with its arrears as compared with the earlier experiments, and this stage is virtually identical with stage 6 of figure 3. From that stage the descent naturally follows the same course as in the preceding series, and in fact only two more stages were examined experimentally to verify this, the final stages of figures 6 and 7 being repeated from figures 3 and 4. The arbitrary unit of time,  $t_0$ , in figure 7 is the same as that in figure 4.

In part I of this series (1) it was shown that the water table in a shallow soil

is higher than that in a deep soil, for the same steady rainfall rate, the reason being that the shallow soil offers the more restricted flow path and therefore demands a higher driving potential. Figures 8 and 9 show that in such a case the effect of path restriction is to lengthen the time required for the water table to fall from one stage to the next, as compared with deeper soil. Again, for purposes of comparison, the time intervals are expressed in terms of the same unit  $t_0$  as before. This slowing of the rate of fall is naturally particularly accentuated when the water table is low and the thickness of the permeable zone becomes very small; in other words, the duration of the tail end of the drainage performance is extended more than proportionately to the duration of the initial stages.

To take into account the capillary fringe is an additional complication, as has been explained, and the single case chosen was that of shallow soil, where the influence of the capillary fringe might be expected to be at its maximum. The results are shown in figures 10 and 11, and the difference between the latter and the corresponding figure 9 is explicable in general terms, the same time unit  $t_0$  again being adopted. In the presence of a capillary fringe, the initial rate of fall of the fringe boundary is considerably less than the initial rate in figure 9, since the fringe boundary has a lower potential than has a water table at the same height. Hence, the driving force being less, although the path resistance is approximately the same, the rate of flow is less, and in our circumstances this means that the rate of fall of the boundary is less. In fact, when comparing rates of fall, one should rather expect approximate equality for the same stage of water table than for the same boundary stage. A boundary fall in figures 10 and 11 from a midpoint height of 5 cm. in the analogue to 4 cm. is accompanied by a water table fall from 4 cm. to 3 cm., in a time interval of 5.85  $t_0$ . In figures 8 and 9 the water table at the midpoint falls from the 4-cm. height to the 3-cm. height in 5.33  $t_0$ . This is not very different, but the time of fall from the 5-cm. height to 4 cm. is only 4.92  $t_0$ . In spite of this early disadvantage caused by the capillary fringe, the time taken to approach the ultimate steady state with the water table at drain level is very much reduced, because the capillary fringe provides an appreciable flow path right to the end.

Though we are justified in assuming the same value of  $t_0$  in figure 11 in order to discuss a difference in *shape* of curve, in fact the very presence of a capillary fringe indicates a real soil difference and therefore a difference of the absolute time scale. If we proceed to estimate the absolute time scale in the same manner as when discussing figures 3 and 4, and choose our scale to give a drainage system of the same dimensions as on the earlier occasion, we find that the capillary fringe thickness is about 50 cm. It will be observed that this thickness remains almost constant throughout the descent of the water table, in spite of the steady decrease of flow rate which, in principle, should have some slight effect in diminishing the fringe thickness (3). A fringe thickness of such dimensions corresponds to a sand with particle size of about 0.1 mm., which would have a permeability of about  $10^{-6}$  c.g.s. units. This yields  $t_0 = 9.45$  hours as the appropriate interpretation of figure 11, from which we see that the whole course of that figure is run in about 12 days.

It only remains to add to this part of the discussion that, since the water released by the soil, as the saturated zone boundary falls, flows to the drain, it is clearly a simple matter to calculate, from the curves shown, the rate of flow per unit length of drain and its variation with time. It is hardly necessary to illustrate this by an example.

This is a convenient moment to review once again the strictly mathematical approach to our problem. Since this was last discussed, in part II (2) of this series, a notable advance has been made by Gustafsson (4), but at the same time our requirements have increased. In part II we developed the hodograph of a drainage cross section, with finite drain dimensions and with rainfall incident at the water table, and the difficulties of further progress were self-evident. Gustafsson's advance was made possible by three separate novel considerations. He first dealt with the case of drainage of artesian water emanating from an infinitely deep aquifer. Having solved this problem, he superimposed a uniform vertically downward flow, which introduced a rainfall element at the water table and was chosen just to eliminate the artesian flow at depth. The result was the solution of the problem of the drainage of local rainfall water. The second step was to assume the drain to be of infinitesimally small diameter, requiring an infinitely great negative potential and an infinitely great velocity of flow of water at the drain perimeter. This gives us the drainage boundary cross section shown in figure 12 from which, by applying the principles described in part II, we can derive the form of the hodograph shown in figure 13. By a series of transformations, which are equivalent to the single transformation

$$v_1 = \{(v + ik)/v\}^2$$

where  $v$  is the variable of the hodograph plane, namely, the velocity of water flow at the corresponding point  $(x, y)$  of figure 12,  $k$  is the permeability, and  $i$  is  $\sqrt{-1}$ . We then arrive at figure 14; in this diagram it is seen that the artesian source  $FG$  and the drain "sink"  $DE$  have been carried through and result in point source  $F''G''$  and point sink  $D''E''$  respectively, on an upper half plane which is isolated from the lower except for the leakage gap  $P''B''$ . Gustafsson's third step was to close this gap arbitrarily, making  $B''$  coincide with  $P''$ , or, in the hodograph plane, choosing the hodograph of the free surface to be the complete semicircle  $A'P'$ . This is justifiable, but results, of course, in a solution for only a particular case, which may or may not turn out to be one with which we are concerned. As a result of this assumption, the problem is reduced to that of flow between a point source and a point sink on the real axis of the half plane, the solution of which is well known. Final transformation back to the plane of figure 12 yields the solution.

It is desirable to point out that the solution is that of a particular case, since Gustafsson does not present it as such; it is a minor detraction from the most promising development yet published. A second criticism is that in practice drains are not infinitesimally small and could not be maintained at an infinitely great negative potential even if we would. The answer to this is that we may choose from the flow not any equipotential surface and take that as our drain perimeter containing water at the potential indicated. This is not an entirely

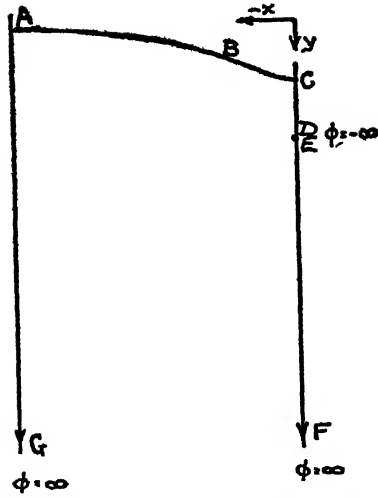


FIG. 12. DRAINAGE BOUNDARY CROSS SECTION  
See text for details

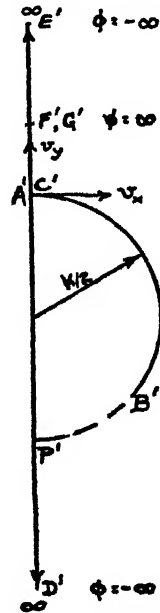


FIG. 13. HODOGRAPH DERIVED FROM FIGURE 12  
See text for details

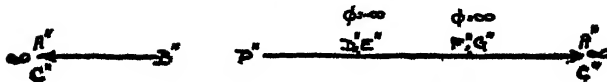


FIG. 14. FURTHER TRANSFORMATION OF FIGURE 13  
See text for details

satisfying answer, since it is a formidable matter to calculate equipotential surfaces from the complete solution, and those presented by Gustafsson were, in fact, drawn in freehand by personal judgment. And even if it were done, there is no guarantee that our solution would correspond to a reasonable drain section at a reasonable potential.

Finally, our demands now extend beyond a solution of the problem for steady uniform rainfall. For constructing the sequence of water tables after a change of rainfall rate we must be able to obtain a solution when the flux across the water table is nonuniform. Much as we should all desire a satisfying mathematical solution, and much as we may admire the ingenuity and dexterity with which the mathematical approach has been conducted in bringing its exponents to their present advanced position, it appears that the electric analogue is still the only sure alternative to the small-scale model using actual permeable materials and fluids.

#### SUMMARY

The method of electric analogues as applied to drainage problems is extended to deal with the case of a rising or falling water table, that is, to the unsteady state following changes of rate of rainfall, with a system of equidistantly spaced drains. It is shown that, over a very considerable range of movement following cessation of rain, starting from a steady state and continuing until the water table is but little higher than the drain level, the water table falls as a whole without appreciable change of shape, after which it naturally falls more slowly over the drain line than elsewhere, since the distance left to fall is smaller. The relation between water-table height and time is shown for various horizontal distances from the drain. The water table approaches drain level asymptotically but not, except fortuitously, exponentially, since the height-time curve has a different shape for each distance from the drain line. Over the range where the water table falls without change of shape, it also rises without change of shape when rainfall is resumed. Consequently, the average water table during the period of fluctuation coincides with the water table for a steady rainfall of some average intensity, always provided that the movement is not carried outside this range.

When the initial state is that of saturation to the soil surface instead of a steady state corresponding to constant rainfall, cessation of rainfall is followed at first by a faster fall of water table over the drainline than elsewhere, after which the movement repeats the course followed in the first-mentioned circumstances.

The water table falls more slowly in a shallow soil than in a deeper soil, other factors being the same.

The shape of the height-time curve for the water table or capillary fringe boundary depends on the thickness of the capillary fringe, particularly when the soil is shallow. If the fringe is of appreciable thickness, the ratio of the initial rate of fall to the rate of fall when the water table is at some specified small height above the drains is lower than when the fringe is of negligible thickness. This is due mainly to the fact that the capillary fringe provides a flow path of appreciable thickness even when the water table is at drain level, which may be

the level of the impermeable bed. Thus the tail end of the drainage performance may be completed more freely than when the capillary fringe is absent.

A recent advance in the mathematical theory of our problem is examined, and is shown to apply only to a particular case. This very considerable advance is limited to the case of uniformly distributed steady rainfall, and therefore cannot be adapted to the case of the rising or falling water table.

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# ANION EXCHANGE IN SOILS: I. EXCHANGEABLE PHOSPHORUS AND THE ANION-EXCHANGE CAPACITY

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The anion-exchange reactions of soils may be described as the substitution of one anion by another which is present in solution in greater concentration or possesses a stronger tendency to hold its position on the soil. Soils which do not have excessive amounts of calcium or magnesium in the system take up, or "fix," large amounts of phosphorus by the substitution of phosphate ions for hydroxyl ions (5, 9, 16). Conversely, phosphate ions which have become affixed to soils by this means can be displaced by hydroxyl, fluoride, and possibly other anions (3, 6, 14, 16). Tentative methods for the determination of exchangeable phosphorus and the total anion-exchange capacity have been suggested by Piper (12). It is apparent, however, that the anion-exchange reactions of soils are not strictly analogous to the base-exchange reactions.

The phosphorus which accumulates in acid soils as a result of intensive fertilization is, for the most part, relatively insoluble in dilute solutions of the strong mineral acids but can be readily replaced from soils by solutions containing certain anions. The majority of the common procedures for evaluating the phosphorus fertility status of soils are based on solubility, rather than on an anion-exchange reaction. Thus, much of the phosphorus which has accumulated in fertilized soils is not considered when evaluating the phosphorus fertility. Burd and Murphy (3) have suggested that this absorbed phosphorus should be considered when chemical data are used in the prognosis of phosphate deficiency in soils.

In this investigation an attempt has been made to determine whether a soil has a more or less definite anion-exchange capacity, and to consider the mechanism of the reaction. Attention was also given to the properties of the exchangeable phosphorus in soils.

## THEORETICAL CONSIDERATIONS

Mechanisms for the reactions involved in the taking up of phosphorus by soils have been frequently postulated. There seems, however, to be no acceptable generalization. In order to simplify this discussion the reactions which involve calcium and magnesium are not considered. Chemical precipitations, adsorption phenomena, and anion exchange have all been advanced as mechanisms by which phosphate is fixed by soils. In this discussion of anion exchange it is not the authors' intention to imply that it is the only mechanism by which phosphates are fixed by soil.

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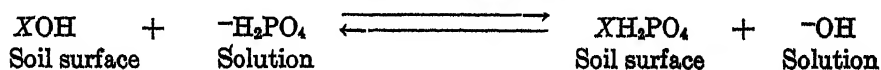
The formulation of some hypothesis explaining the mechanism of these reactions necessarily precedes any detailed investigation. The following concepts were considered at the outset of these studies and were useful in the interpretation of the experimental results.

Kolthoff (10) has recognized two types of exchange reactions: the exchange of counter ions and the exchange-adsorption of lattice ions.

Counter ions are held in an extra-lattice position at the surface of crystals as a result of unequal distribution of forces within the crystals. The exchangeable cations of soils are predominately counter ions, and the relative adsorbability of the different cations by the clay minerals is related to valence charge and ionic size.

The exchange-adsorption of lattice ions involves the lattice ions which are at the corners or edges of certain ionic crystals. These ions are less restricted than similar ones on the plane surfaces and within the crystals. Kolthoff and co-workers have shown that these less restricted lattice ions may enter into exchange reactions with ions in the surrounding solution. For example, when crystalline barium sulfate is placed in a solution containing chromate ions there is an equivalent exchange between some of the lattice sulfate ions on the surfaces of the barium sulfate and the chromate ions in solution. In this instance there is an isomorphic replacement, the foreign ion fits into the lattice of the adsorbent, and its size is of the same magnitude as that of the replaced ion. Other examples of exchange reactions of this nature are available, however, which are not limited by the similarity of size or valence charge of the exchanging ion and the exchanged lattice ion.

It is conceivable that the anion-exchange reactions of acid soils are analogous or similar to the exchange-adsorption of lattice ions just described. For example, when phosphorus is adsorbed (fixed) there is an exchange between certain of the hydroxyl ions of the clay minerals or hydrous oxides and the phosphate ions in solution in accordance with the following reaction:



It is well known that certain species of anions such as sulfates, chlorides, and nitrates are adsorbed to only a limited degree by soils. There is apparently no satisfactory rule that will permit predictions regarding the adsorbability of anions. At first sight it would appear that the adsorbability of anions would increase with decreasing solubility of the compound formed between the adsorbed ion and the lattice ion of opposite charge. Such a basis might well explain why phosphates but not chlorides are adsorbed by soils. This, however, does not explain the strong adsorption of the fluoride ion. Apparently, depending on the situation, there are other operative factors.

#### ✓METHODS

The tentative method for determining the anion-exchange capacity of soils suggested by Piper (12) is essentially a counterpart of the usual methods em-

ployed for determining the base-exchange capacity. According to this method, soil samples are saturated with phosphate by treating with *N* ammonium phosphate solution at pH 4. After the excess phosphate solution has been removed by washing with alcohol, the adsorbed phosphate is removed with sodium hydroxide and subsequently determined.

In this investigation it was sought to determine the anion-exchange capacity of soils with respect to several different combinations of anions. Only a brief description of the methods employed are given here. A detailed description of the methods used is given in an accompanying paper (13). A value of 5.7 was chosen as the reference pH at which the anion-exchange adsorption capacity was determined. There was no real theoretical basis for selecting this particular pH value except that many of the solutions employed were well buffered at this point. A pH of 5.7 is also fairly representative of acid agricultural soils.

The essential features of the method used to determine the anion-exchange capacity of soils with different combinations of anions were as follows:

1. Samples were pretreated with 0.5 *M* sodium acetate at pH 5.7 to remove the divalent cations and to bring all soil samples to the same pH.
2. The samples were then treated with a 0.5 *M* solution, pH 5.7, of the sodium salt of the anion desired for saturation (phosphate, arsenate, or other).
3. The excess saturating solution was removed by washing the samples with alcohol.
4. The anion absorbed by treatment 2 was displaced by treating the samples with a 0.5 *M* solution, pH 5.7, of the sodium salt of another anion.

The amount of anion adsorbed and displaced in this manner was considered to be the anion-exchange capacity.

When soils are treated with solutions containing phosphates or certain other anions, the adsorption of these anions at room temperatures is not instantaneous; commonly many days are required to establish what approximates an equilibrium. Experience seemed to indicate that two half-hour heatings in a boiling water bath brought most soils to approximate equilibrium with the extracting solutions.

#### ALTERNATE SATURATION OF SOILS WITH ARSENATE AND PHOSPHATE IONS

At the outset of this investigation further data were sought to demonstrate whether soils have a definite anion-exchange capacity. To this end, 12 soils were saturated with arsenate, the adsorbed arsenate was displaced with phosphate, and the adsorbed phosphate, in turn, was displaced by arsenate. The results (table 1) demonstrate the alternate saturation of soils with arsenate and phosphate ions. The anion-exchange capacities of the soils are of similar magnitude to the base-exchange capacities.

The amounts of arsenate and phosphate ions adsorbed and subsequently displaced from the same soil were not the same; in all cases more phosphate than arsenate was displaced. The molar ratio of phosphate to arsenate ions adsorbed varied from 1.25 to 2.62. In a solution at pH 5.7 approximately 90 per cent of the phosphate ions are monovalent ( $\text{H}_2\text{PO}_4^-$ ), whereas in an arsenate solution at the same pH, 95 per cent of the ions are divalent ( $\text{HAsO}_4^-$ ). If the valence

affects the number of anions that are adsorbed by soils, then it is possible to have 1.8 times more phosphate than arsenate ions adsorbed at pH 5.7. On the other hand, since the phosphate ions are considerably smaller than the arsenate ions, there may conceivably be positions on the surface of crystals where phosphate ions could be adsorbed to the exclusion of arsenate.

#### EXCHANGEABILITY OF ANIONS ADSORBED BY SOILS

Experimental data were next obtained to show how completely the phosphorus of a soil saturated with phosphate ions can be displaced by solutions of other anions. Samples of a series of eight soils were saturated with phosphate and subsequently treated with 0.5 *M* solutions of sodium arsenate, citrate, tartrate, acetate, and ammonium fluoride, and with 0.125 *N* sodium hydroxide. With the exception of the sodium hydroxide solution, all solutions were adjusted to

TABLE 1

*Arsenate and phosphate retained by soils after alternate saturation with phosphate and arsenate ions*

Results in millimols per 100 gm.

SOIL NO.	SOIL TYPE	ARSENATE ADSORBED	PHOSPHATE ADSORBED	RATIO $\text{PO}_4/\text{AsO}_4$
E959	Caribou loam	9.6	12.0	1.25
E1141	Sassafras loam	3.9	6.4	1.64
E1171	Sassafras loamy sand	1.3	2.1	1.62
E1753	Collington loam	6.1	9.5	1.56
E1568	Sable silty clay	6.1	16.0	2.62
C4745	Brookston clay	4.7	9.9	2.11
C4746	Wooster silt loam	3.7	6.3	1.70
E1644	Portsmouth fine sandy loam	4.0	7.1	1.78
E1645	Lynchburg fine sandy loam	1.9	2.2	1.16
E787	Davidson clay loam	10.0	16.0	1.60
C4740	Cecil sandy clay loam	4.1	6.5	1.58
E1824	Hawaiian clay	30.0	41.0	1.37

pH 5.7. The total adsorbed phosphorus was estimated by determining the total phosphorus in one set of phosphate-saturated soils and subtracting from these values an estimate of nonexchangeable phosphorus (total phosphorus of untreated soils minus the exchangeable phosphorus).

The data (table 2) show that the extractions with the citrate and hydroxyl solutions removed all of the adsorbed phosphate. The fluoride removed all of the adsorbed phosphorus from the five soils having a low anion-exchange capacity and almost all from the three soils having a high capacity. The arsenate and tartrate removed only a part of the total adsorbed phosphate; relatively less was removed from the soils having high amounts of adsorbed phosphate. As was expected, the acetate removed the least adsorbed phosphorus, and these amounts are probably similar to what could be extracted by hydrolysis with hot water.

Also included in table 2 are the total adsorbed phosphorus and anion-exchange

capacity when the soils were saturated in accordance with the Piper method (12). The lower amount of phosphorus adsorbed by this method is probably due to the use of a less rigorous heat treatment and a phosphate solution of lower

TABLE 2  
*Phosphate displaced from phosphate-saturated soils by solutions of other anions*  
Results in millimols per 100 gm.

SOIL NO.	SOIL TYPE	TOTAL PHOSPHORUS ADSORBED	PHOSPHORUS DISPLACED BY						SOILS SATURATED BY PIPER METHOD	
			Arsenate	Fluoride	Hydroxyl	Citrate	Tartrate	Acetate	Total phosphorus adsorbed	Phosphorus exchanged by hydroxyl
E1908	Atwood fine sandy loam	5.4	4.1	5.5	6.4	5.4	5.1	2.9	4.0	3.9
E1783	Collington sandy loam	8.5	5.0	8.3	9.4	8.5	7.2	3.1	6.0	6.7
E1645	Lynchburg fine sandy loam	5.1	5.4	6.5	7.4	7.2	7.2	3.4	6.0	6.7
E1141	Sassafras loam	15.8	9.1	14.5	18.4	15.5	11.5	4.9	12.8	10.1
E1644	Portsmouth fine sandy loam	14.7	9.2	14.4	14.9	14.8	13.4	6.1	10.9	10.4
E1911	Chester clay loam	25.7	13.8	21.3	28.5	24.4	14.7	8.0	14.9	14.9
E787	Davidson clay loam	32.0	15.6	27.6	32.2	30.2	18.5	10.4	20.3	19.7
E959	Caribou silt loam	32.3	16.2	24.5	33.6	31.4	18.4	8.8	20.1	19.7

TABLE 3  
*Arsenate, fluoride, and tartrate retained by soils as exchangeable anions*  
Results in millimols per 100 gm.

SOIL NO.	SOIL TYPE	ARSENATE-SATURATED SOILS		FLUORIDE DISPLACED FROM FLUORIDE-SATURATED SOILS BY PHOSPHATE	TARTRATE DISPLACED FROM TARTRATE-SATURATED SOILS BY PHOSPHATE
		Total arsenate	Arsenate displaced by phosphate		
E1908	Atwood fine sandy loam	2.3	3.8	11.2	1.6
E1783	Collington sandy loam	2.7	2.8	13.4	1.2
E1645	Lynchburg fine sandy loam	....	1.9	13.5	1.9
E1141	Sassafras loam	4.9	3.9	15.5	1.8
E1644	Portsmouth fine sandy loam	4.3	4.0	14.3	5.3
E1911	Chester clay loam	9.1	10.0	15.5	3.7
E787	Davidson clay loam	11.2	10.0	12.3	5.4
E959	Caribou silt loam	12.5	9.6	18.0	4.5

concentration to saturate the soils. The relative values for the different soils, however, are apparently in no way impaired.

Additional data concerned with the relative amounts of anions retained and displaced from soils by other anions are contained in table 3. Comparison of the

first columns of tables 2 and 3 indicates that about half as much arsenate as phosphate is adsorbed by the same soils. Apparently all of the adsorbed arsenate is displaceable with phosphate.

The amount of fluoride displaced from the fluoride-saturated soils by phosphate (table 3) was apparently independent of the anion-exchange capacity. It is probable that with the methods of saturation employed, fluorine has combined or reacted rather actively with the soils. For this reason, it was concluded that the fluorine displaced from fluoride-saturated soils will not be indicative of the anion-exchange capacity.

The role of organic anions such as citrate and tartrate in the anion-exchange reactions of soils has not been definitely clarified. It has long been known that citric acid is an effective reagent for extracting phosphates from soils. There is no direct evidence, however, that appreciable amounts of citrate ions are adsorbed by soils. Steele (15) has shown that citrates, oxalates, and humates are effective in reducing the adsorption of phosphates by soils. Data in table 3 show that when soils are treated with 0.5 *M* sodium tartrate, pH 5.7, relatively small amounts of tartrate are adsorbed which can subsequently be displaced with phosphate. An attempt to obtain similar data with citrates was unsuccessful because of analytical difficulties. The indications were that only relatively small amounts of citrate ions are adsorbed by soils as exchangeable anions.

#### CLAY CONTENT OF SOILS AND THE ANION-EXCHANGE CAPACITY

If the anion-exchange reactions of soils involve lattice ions at the corners and edges of crystals, then it would follow, other things being equal, that soils having the greatest percentage of clay or the highest specific surface would have the highest anion-exchange capacities. It was found that the anion-exchange capacities of a series of Sassafras soils from Long Island and Virginia varied between the limits of 1.3 and 9.8 millimols per 100 gm. The clay contents of these soils (table 4) show a fairly consistent positive correlation with the anion-exchange capacities. The specific surface (11) was determined on seven of the soils, and here again there was the tendency for the soils of high specific surface to have the higher anion-exchange capacities.

#### REMOVAL OF FREE IRON OXIDES AND THE ANION-EXCHANGE CAPACITY

The discussions, thus far, concerned with the mechanism of the anion-exchange reactions have not associated these reactions with any specific mineral or crystal structure. The kaolin minerals and certain of the hydrous oxides of iron and aluminum have been shown to adsorb phosphorus. The release of hydroxyl ions which has been observed to accompany the adsorption of phosphates has been considered as evidence of anion exchange. In accordance with the observations of Hendricks (7), it is probable that the site of the exchangeable hydroxyl ion of the kaolin minerals is on the lateral faces.

Several studies have shown that the treatment of colloids or soils to remove the free iron oxides substantially reduces the adsorption of phosphates (1, 4, 17). The results of these studies have been taken to support the contention that in

acid soils the adsorption of phosphates is primarily due to the formation of insoluble iron compounds. When a biological reduction of the iron (1) is employed, the effect on the adsorption of phosphates is not so pronounced.

The series of eight soils which had previously been studied were treated chemically by the method of Truog *et al.* (18) to remove the free iron oxides. The anion-exchange capacities of the treated soils were determined by two methods: first arsenate displaced by phosphate, and second, phosphate displaced by fluoride. The data (table 5) show a substantial reduction in anion-exchange capacity as a result of the treatment for all but one soil. An explanation for the increase in exchange capacity of the Portsmouth soil is that the sulfides may not

TABLE 4

*Relationship between anion-exchange capacity of Sassafras soils and percentage clay or specific surface\**

SOIL NO.	ANION-EXCHANGE CAPACITY	CLAY <0.002 MM.	SPECIFIC SURFACE
	<i>millimols 100 gm.</i>	<i>per cent</i>	<i>sq. m./gm.</i>
D4531	1.3	3.7	0.698
D4533	1.8	5.7	1.545
D4521	3.0	7.4	3.88
D4519	3.6	8.1	
D4511	4.1	9.3	
D4515	4.4	7.6	
D4516	4.7	9.0	3.78
D4513	4.9	10.4	
D4522	4.9	11.5	
D4524	5.0	10.1	
D4521	5.1	10.1	
D4514	5.6	9.4	
D4512	6.2	11.2	5.44
D4517	6.9	11.4	
D4520	7.4	14.0	6.99
D4518	9.8	10.2	5.81

\*The clay and specific surface measurements were made by the mechanical analysis laboratory and by R. A. Nelson, respectively.

have been completely removed. The amounts of iron removed from the soils do not seem to be related to the reduction in anion-exchange capacity.

It does not necessarily follow from the foregoing results that all of the reduction in anion exchange-adsorption capacity is directly attributable to removal of iron oxide. The chemical treatment was drastic enough to destroy other crystal structures in addition to the iron oxides. In any case, the adsorption of phosphate by anion exchange appears to be a reversible phenomenon.

#### DISPLACEMENT OF EXCHANGEABLE PHOSPHORUS

Presumably, during the process of saturating a soil with anions such as arsenate or fluoride, the exchangeable phosphorus which the soil contained is displaced

and may be determined in the extract used for saturation. Since marked differences were found in the amounts of total adsorbed phosphorus exchangeable by the different anions, it appeared desirable to see whether similar differences also occurred when the exchangeable phosphorus of soils was determined. Consequently, the series of eight soils were extracted with 0.5 *M*, pH 5.7, solutions of arsenate, fluoride, tartrate, and citrate and with 0.125 *N* sodium hydrox

TABLE 5  
*Effect of removal of free iron oxides on the anion-exchange capacity*

SOIL NO.	SOIL TYPE	UNTREATED SOILS		SOIL TREATED TO REMOVE FREE IRON OXIDES*		
		Arsenate displaced by phosphate	Phosphate displaced by fluoride	Arsenate displaced by phosphate	Phosphate displaced by fluoride	Fe <sub>2</sub> O <sub>3</sub> removed
		mmols./100 gm.	mmols./100 gm.	mmols./100 gm.	mmols./100 gm.	per cent
E1908	Atwood fine sandy loam	3.8	5.5	1.4	2.3	1.02
E1783	Collington sandy loam	2.8	8.3	1.1	1.3	1.76
E1645	Lynchburg fine sandy loam	1.9	6.5	1.2	1.2	0.21
E1141	Sassafras loam	3.9	14.5	2.0	3.5	1.71
E1644	Portsmouth fine sandy loam	4.0	14.4	18.8	18.2	0.36
E1911	Chester clay loam	10.0	21.3	2.2	3.4	3.29
E787	Davidson clay loam	10.0	27.6	7.9	14.3	8.02
E959	Caribou silt loam	9.6	24.5	1.4	2.8	3.24

\* The writers are indebted to A. J. MacKenzie for these data.

TABLE 6  
*Exchangeable phosphorus displaced from natural soils with different reagents*  
Results in millimols per 100 gm.

SOIL NO.	SOIL TYPE	EXCHANGEABLE PHOSPHORUS REPLACED BY					TOTAL PHOSPHORUS
		Arsen- ate	Fluor- ide	Hy- droxyl	Tar- trate	Cit- rate	
E1908	Atwood fine sandy loam	0.24	0.24	0.29	0.16	0.29	0.71
E1911	Chester clay loam	0.36	0.43	0.58	0.17	0.36	1.73
E787	Davidson clay loam	0.56	0.66	0.84	0.20	0.40	2.63
E959	Caribou silt loam	1.21	1.14	1.85	1.18	1.79	3.35
E1644	Portsmouth fine sandy loam	1.38	1.77	1.58	1.50	1.85	2.75
E1141	Sassafras loam	1.70	1.99	2.38	1.54	2.21	3.95
E1783	Collington sandy loam	1.76	2.18	2.49	1.84	2.36	3.57
E1645	Lynchburg fine sandy loam	1.86	2.40	2.36	2.10	2.65	3.12

ide. The phosphorus in these extracts was determined, and the results are reported as exchangeable phosphorus in table 6.

The Atwood, Chester, and Davidson soils contained relatively low amounts of exchangeable phosphorus. These three soils probably have received little or no phosphatic fertilizers. The other five soils have been heavily fertilized, and a large percentage of their total phosphorus is exchangeable. The hydroxyl

and citrate solutions extracted the largest amounts of exchangeable phosphorus, with the fluoride in most instances extracting almost as much. On the soils containing the higher amounts of exchangeable phosphorus, the arsenate and tartrate solutions extracted low amounts of exchangeable phosphorus as compared with the other anions.

#### DISCUSSION

The data presented in the foregoing sections lend support to the contention that soils treated by techniques which are essentially a counterpart of the base-exchange methods show a definite anion-exchange capacity. The different species of anions, however, are not adsorbed by soils to the same degree. For example, there is about twice as much phosphate adsorbed as an exchangeable anion as there is arsenate. Also, arsenate will not displace all of the phosphate adsorbed by soils, whereas phosphate will displace all of the adsorbed arsenate. These and other observations indicate that the ionic and other properties are involved in governing the amounts of anions adsorbed in the exchangeable form. The factor of ionic size, however, does not preclude the presumed necessity for a chemical affinity between each particular species of anion and the metallic ions of the active crystal surfaces which take part in the anion-exchange reactions. It would be of interest to know whether it is the same surfaces or crystal lattices that adsorb more of the smaller ions than of the larger anions, or whether this phenomenon is the property of specific classes of materials which will adsorb one species of anion but not another. Possibly a study that utilized materials of known composition such as the kaolin minerals and the hydrous oxides would be helpful in this regard.

When soils are partly saturated with phosphate under natural conditions (by the long-continued use of phosphatic fertilizer in the field), apparently the exchangeable phosphorus is for the most part as readily replaceable with arsenate as with the small anions such as fluoride (see table 6); whereas when soils are fully saturated under rather drastic laboratory conditions, only about half of the adsorbed phosphate is replaced by arsenate (see tables 2 and 3). This tends to place a greater importance on those soil surfaces that have the property of adsorbing large as well as smaller ions.

The efficiency of the sodium citrate solution in removing the adsorbed or exchangeable phosphorus from soils is difficult to explain. It is not improbable that the mechanism involved is something apart from an anion-exchange reaction *per se*. There is no evidence available which demonstrates that citrate ions are adsorbed by soils. Fertilizer chemists have found iron oxide and iron and aluminum phosphates to be appreciably soluble in neutral ammonium citrate (2, 8). It seems likely that the solvent action of citrate solutions involves the formation of complex ions.

The data presented in this paper should be helpful in the consideration of possible methods of determining the anion-exchange capacity and the exchangeable phosphorus of soils. It is evident that extraction with hydroxide or fluoride solutions will give a satisfactory estimate of the exchangeable phosphorus.



Citrate may also be equally satisfactory; however, high results may be obtained with certain soils, especially if these contain calcium phosphates. It is quite evident that any estimate of the anion-exchange capacity will be more or less empirical. The concentration and pH of the solution used to saturate soils and the method of saturation must all be carefully standardized. Since a soil phosphate problem is likely to be the dominant reason for desiring the evaluation of anion-exchange capacity, the use of phosphate-saturated soils would appear to be most logical. Although in the past this laboratory has evaluated the anion-exchange capacity of a large number of soils, using arsenate-saturation, this practice will probably not be continued in the future.

#### SUMMARY

Recent experimental evidence has supported the contention that anion exchange is the mechanism causing much of the phosphorus retention of acid soils. Accordingly, a study of the anion-exchange properties of soils was made. The results of this study may be summarized as follows:

Soils were shown to have an anion-exchange capacity in that they can be alternately saturated with arsenate and phosphate ions.

When comparable methods of saturation are employed, more phosphate than arsenate is always retained by soils as exchangeable anions.

The phosphorus retained by soils as an exchangeable anion is virtually completely removed by fluoride, hydroxide, and citrate solutions, but anion exchange is probably not involved when adsorbed phosphates are extracted from soils by citrate solutions.

The anion-exchange capacity of a series of Sassafras soils was shown to increase with increasing clay content or specific surface.

Soils treated chemically to remove the free iron oxides had a reduced anion-exchange capacity; however, this reduction in exchange capacity was not proportional to the amounts of iron dissolved from the soils.

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# ANION EXCHANGE IN SOILS: II. METHODS OF STUDY

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For several years the writers have been considering the anion-exchange reactions of soils. The methods used for saturating soils with anions and for displacing the adsorbed anions were virtually a counterpart of the common base-exchange methods. Since operations of this type involving anions rather than cations are not in common usage, it was necessary to alter existing methods to meet these new requirements. The purpose of this paper is to describe the salient features of the methods that were found to be satisfactory in the study of the anion exchange of soils.

## COMMON OPERATIONS AND REAGENTS

### *Methods of extraction and saturation*

The usual procedures used for leaching soils in base-exchange studies were found to be unsatisfactory when applied to anion exchange. Soils treated with strong phosphate, arsenate, or similar solutions become dispersed, making filtrations tedious if not impossible in certain instances. For this reason, all extractions were made by a decantation method using centrifugal force to separate the two phases.

Soil samples of appropriate size (usually 5 gm.) were placed in 100-ml. centrifuge tubes, and 50 ml. of extracting solution was added. The contents of the tubes were then stirred several times with individual stirring rods during about 5 minutes. If heat treatments were to be given, the tubes were at this point immersed in a boiling water bath for the prescribed period. The tubes were then centrifuged for 15 minutes at a relative centrifugal force of approximately 700 times gravity, and the supernatant liquid was decanted. For a complete extraction the entire process was usually repeated at least four times; thus, each soil sample was treated with a minimum of 200 ml. of solution.

### *Alcohol washing*

In preparing a soil saturated with a given anion for the purpose of determining the anion-exchange capacity it is necessary to remove the excess of the solution used for saturation. An inherent difficulty with washing saturated soils is loss by hydrolysis, and if hydrolysis is prevented by the use of alcohol there is the possibility of precipitating salts in the soils. As a compromise the following washing procedure was adopted:

After the last of the saturating solution had been decanted, 25 ml. of water was added to each of the tubes, and the contents were stirred. Then 25 ml. of 95 per cent ethyl alcohol

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was added, the contents of the tube again were stirred, and after centrifugation the alcohol was decanted. Three additional washings were then made with 50 ml. of 95 per cent alcohol. Frequently, after the fourth washing was centrifuged, the supernatant liquid was found to be cloudy. When this occurred, two drops of sodium acetate solution was stirred into the supernatant liquid, and the tube was recentrifuged.

### *Decoloration of soil extracts*

Invariably when soils are treated with phosphate, arsenate, or similar solutions, sufficient soil organic matter is removed to give dark-colored extracts. Unless removed, this organic matter interferes with the analysis of the extracts.

The extracts were made to a volume of 250 ml., and about 75 ml. was then transferred to a 125-ml. flask containing 1 gm. of activated charcoal (Darco G 60). The contents of the flasks were mixed by swirling, allowed to stand for a few minutes, and filtered through Whatman No. 42 paper, the first 10 ml. of filtrate being discarded.

### *Reagents*

*0.5 M sodium acetate, pH 5.7*—41 gm. of anhydrous sodium acetate was dissolved in a liter of water and adjusted to pH 5.7 with glacial acetic acid.

*0.5 M sodium phosphate, pH 5.7*—69 gm. of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  was dissolved in 900 ml. of water, the solution adjusted to pH 5.7 with sodium hydroxide, and finally diluted to 1 liter.

*0.5 M sodium arsenate, pH 5.7*—An approximately saturated solution of arsenic acid was prepared by adding 500 gm. of C.P.  $\text{As}_2\text{O}_5$  to 800 ml. of water and allowing the material to stand for at least 24 hours, then decanting the supernatant liquid. A 50-ml. aliquot of this solution was titrated electrometrically to pH 4.5 and to pH 5.7 with 1.00 *M* sodium hydroxide. The exact molarity of the strong arsenate solution was calculated from the amount of alkali necessary to bring the aliquot to pH 4.5, assuming the formation of  $\text{NaH}_2\text{AsO}_4$ . Thus, the molarity of the strong  $\text{As}_2\text{O}_5$  solution and the amount of sodium hydroxide required to bring it to pH 5.7 being known, a solution of sodium arsenate 0.5 *M* in respect to arsenic and having a pH of 5.7, was prepared.

All samples of C.P.  $\text{As}_2\text{O}_5$  examined contained impurities, a considerable fraction of which were removed by preparing the saturated solution as described. Failure to remove these impurities hampered subsequent determination if this solution was used to extract exchangeable phosphorus from soils.

*0.5 M ammonium fluoride, pH 5.7*—18.5 gm. of ammonium fluoride was dissolved in a liter of water and, if necessary, adjusted to pH 5.7 with ammonium hydroxide. Unless this solution is stored in a wax-lined container, the pH will slowly rise.

*0.5 M sodium citrate, pH 5.7*—96 gm. of citric acid was dissolved in 500 ml. of water, neutralized to pH 5.7 with 20 per cent sodium hydroxide, and diluted to 1 liter.

*0.5 M sodium tartrate, pH 5.7*—75 gm. of tartaric acid was dissolved in 500 ml. of water; 40 gm. of sodium hydroxide was dissolved in 200 ml. of water and poured into the tartaric acid solution. The resulting solution was cooled, adjusted to pH 5.7 with dilute sodium hydroxide, and diluted to 1 liter.

### PRETREATMENT OF SOILS

All of the soil samples used for anion-exchange studies were pretreated by an extraction with 200 ml. of the 0.5 *M* sodium acetate solution, pH 5.7, to remove the divalent bases and to bring the soil samples to the same pH. The removal of the active divalent bases from the soil samples appeared desirable in order to eliminate their role in the retention of anions. If soils containing appreciable

amounts of exchangeable calcium were saturated with an anion for the purpose of determining the anion-exchange capacity, it is conceivable that appreciable amounts might be retained in combination with the calcium rather than as an exchangeable anion. The importance of working with soils having about the same pH cannot be overemphasized.

The validity of determining the exchangeable phosphorus in soils that have been pretreated is debatable. Measurements made in this laboratory have shown the amount of phosphorus extracted by the pretreatment to be very small in comparison with the exchangeable phosphorus, and in most soils the amounts are of negligible importance. On the other hand, if a soil sample is contaminated with fertilizer materials such as monocalcium phosphate, it might be advantageous to remove the contaminant by pretreatment. Studies by Dean (2) have shown that when a base such as sodium hydroxide is used to extract the exchangeable phosphorus, a pretreatment to remove the divalent bases has a marked effect on the amount of phosphorus extracted from certain soils. Apparently this indicates that some of the phosphorus liberated by the sodium hydroxide is reprecipitated by calcium.

#### EFFECT OF CONCENTRATION AND HEAT TREATMENTS ON DETERMINATION OF ANION-EXCHANGE CAPACITY

The amounts of phosphorus adsorbed by soils treated with phosphate solutions depend upon the time of contact and the concentration. The results of Dean and Rubins (3) and Kurtz *et al.* (8) are typical of experiments of this type. For purposes of determining the anion-exchange capacity of soils, therefore, it will be necessary to standardize conditions so as to eliminate these factors as variables and, if possible, establish an equilibrium between the soil and the saturating solution.

The time necessary to establish what approximates an equilibrium can be shortened by applying a heat treatment. The method described by Piper (11) calls for heating soils and saturating solution together at 50–60° C. for 1 to 2 hours. A boiling water bath is preferred by the writers, since it is easier to control. Experience seemed to indicate that two half-hour heatings<sup>2</sup> in a boiling water bath brought most soils to approximate equilibrium with the saturating solution. For example, the data in table 1 show the influence of various heat treatments on the values obtained for the anion-exchange capacity of Davidson clay loam. These data were obtained by saturating the soil with arsenate and displacing the adsorbed arsenate with phosphate. Apparently, if the heat treatment is greatly prolonged the soil breaks down and anion adsorption increases markedly.

On theoretical grounds it is apparent that the effect of concentration becomes of less and less importance as the concentration of the solutions employed for saturating soils with anions is increased. Table 2 compares the anion-exchange capacity values of four soils when 0.25 *M* and 0.5 *M* solutions were used for the

<sup>2</sup> The heatings were used when the soils were being saturated and again when the adsorbed anions were removed.

determinations. These data show consistently higher values when 0.5 *M* solutions were employed. The solutions were sufficiently concentrated, however, to avoid serious discrepancies from small changes in concentration. The 0.5 *M* concentration is advantageous in that the soils remain coagulated to a greater degree, and less centrifuging is necessary to obtain clear extracts.

TABLE 1  
*Effect of heating suspensions of soil and extracting solutions on anion-exchange capacity determinations*

NUMBER OF HEATINGS	TIME OF EACH HEATING	ANION-EXCHANGE CAPACITY
	<i>hours</i>	<i>millimols/100 gm.</i>
None	0	6.1
1	$\frac{1}{2}$	9.3
2	$\frac{1}{2}$	10.5
4	$\frac{1}{2}$	10.8
1	1	10.2
2	1	10.7
4	1	14.4
1	2	11.2
1	4	14.4

TABLE 2  
*Effect of concentration of extracting solutions on anion-exchange capacity determinations*

SOIL NO.	SOIL TYPE	ANION-EXCHANGE CAPACITY DETERMINED WITH:	
		0.25 <i>M</i> Solutions	0.5 <i>M</i> Solutions
		<i>millimols/100 gm.</i>	<i>millimols/100 gm.</i>
E-915	Caribou loam	6.8	9.5
E-1141	Sassafras loam	3.3	3.9
E-787	Davidson clay loam	8.6	10.5
E-1824	Hawaiian clay soil	24.6	30.6

#### PHOSPHORUS DETERMINATION IN SODIUM ARSENATE SOLUTIONS

##### *Reagents*

*Hydrobromic acid*—48 per cent.

*Ammonium metavanadate*—2.345 gm. of  $\text{NH}_4\text{VO}_3$  was dissolved in 500 ml. of hot water, 10 ml. of  $\text{HNO}_3$  (sp.gr. 1.42) added, and the solution diluted to 1 liter.

*Ammonium molybdate*—100 gm. of  $(\text{NH}_4)_2\text{MoO}_4$  were dissolved in 500 ml. of warm water (50° C.) containing 10 ml. of  $\text{NH}_4\text{OH}$  (sp.gr. 0.90). This solution was filtered and diluted to 1 liter.

##### *Procedure*

The arsenate ions were removed from the solution by converting to  $\text{AsBr}_3$  and distilling. To accomplish this, a 10-ml. aliquot of clear solution was placed

in a small Kjeldahl flask (70-ml. capacity), 10 ml. of HBr was added, and the contents of the flask were brought *just* to dryness with moderate heating. The neck of the flask was then washed with 10 ml. of 1.5 *N* nitric acid, and the contents of the flask were boiled gently until colorless. The cooled solution was then transferred to a volumetric flask of suitable size (usually 25 ml.). Sufficient 7.5 *N* HNO<sub>3</sub> was added to make the contents of the flask 1.5 *N* in respect to HNO<sub>3</sub> when diluted to volume (disregarding the 10 ml. of 1.5 *N* HNO<sub>3</sub> added to the Kjeldahl flask).

Mission's vanadomolybdate method (6, 9) was used to determine the phosphorus content of the solution freed of arsenate ions by the method described above. A 10-ml. aliquot was placed in a colorimeter tube; while it was swirling, 1.25 ml. of the metavanadate solution followed by 1.25 ml. of the molybdate solution was added. The yellow color was allowed to develop for 30 minutes before the transmission was measured with a photoelectric colorimeter equipped with a Wratten 420 filter.

### *Comments*

The usual molybdenum blue methods for determining phosphorus were found to be unsatisfactory when applied to solutions freed from arsenic with HBr. Apparently these solutions contain antimony (an impurity in most commercially obtainable arsenates) in sufficient amounts to cause error of a considerable magnitude. The vanadomolybdate method proved to be a very satisfactory substitute. With this method the recovery of standard amounts of phosphorus added to 0.5 *M* sodium arsenate solutions was complete.

### ARSENIC DETERMINATION IN SODIUM PHOSPHATE SOLUTIONS

The method of Cassill (1) was found satisfactory for determining the arsenic in 0.5 *M* phosphate solutions. The solutions analyzed were extracts of arsenate-saturated soils and contained at least 20 p.p.m. of arsenic. The method involves an arsine evolution, absorption in mercuric chloride-gum arabic solution, followed by addition of a measured excess of iodine. The excess iodine is then titrated with standard arsenite. Only minor changes were necessary in adapting this method for use with 0.5 *M* sodium phosphate solutions, pH 5.7. Since these solutions are highly buffered, it was found necessary to increase the evolution period and the amounts of hydrochloric acid and stannous chloride, for production of about 1500 ml. of H<sub>2</sub> during the evolution period is necessary.

### PHOSPHORUS DETERMINATION IN AMMONIUM FLUORIDE SOLUTIONS

The determination of phosphorus by the molybdenum blue reactions in the presence of high concentrations of fluoride ions is greatly simplified if boric acid is used to eliminate the fluoride interference (7). Tests in this laboratory have shown that this use of boric acid will give satisfactory results when the Zinzadze molybdenum blue reagent as modified by Gerritz (5) is employed for the determination of phosphorus.



### Reagents

*Molybdenum blue reagent*—19.6 gm.  $\text{MoO}_3$  and 1.25 gm. of molybdenum metal were dissolved in 500 ml. of concentrated sulfuric acid. [For details on preparing this reagent, see Gerritz (5) or Peech *et al.* (10).]

*Dilute molybdenum blue reagent*—one volume of the above molybdenum blue reagent was diluted with three volumes of water and cooled.

*Sodium bisulfite solution, 8 per cent*—40 gm. of sodium bisulfite (meta, powder) was dissolved in 500 ml. of 1.0 *N* sulfuric acid. A fresh supply was prepared every week.

*Boric acid*—0.8 *M*.

*Quinaldine red*—0.01 per cent aqueous solution.

### Procedure

An aliquot of clarified ammonium fluoride extract containing no more than 2 millimols  $\text{H}_2\text{BO}_3$  and less than 50 gammas phosphorus was transferred to a 50-ml. volumetric flask, and 15 ml. of 0.8 *M* boric acid added. The acidity was adjusted by adding 4 drops of quinaldine red indicator followed by 1 *N* sulfuric acid until the pink color just disappeared. The solution was then diluted with water to 35 ml., and 5 ml. of sodium bisulfite solution was added and the flask placed in a boiling water bath for 40 minutes. Then 2 ml. of freshly prepared dilute molybdenum blue reagent was added, the contents of the flask were mixed by swirling, and the heating was continued for 90 minutes. The cooled solution was made to volume, and the transmittancy measured at 660  $\text{m}\mu$ .

### PHOSPHORUS DETERMINATION IN SODIUM TARTRATE AND CITRATE EXTRACTS

Phosphorus was determined in the sodium tartrate and citrate extracts by the molybdenum blue method after the tartrates and citrates had been destroyed by a modification of the method of Warren and Pugh (12) for determining phosphorus in 1 per cent citric acid extracts.

Three grams of  $\text{KMnO}_4$  was placed in a 70-ml. Kjeldahl flask. Ten milliliters of the clarified citrate or tartrate extract was pipetted into the flask and 1 ml. concentrated  $\text{HCl}$  added without disturbing the flask. After the reaction subsided another small portion of  $\text{HCl}$  was added and this procedure continued until the total added was 10 ml. After standing 30 minutes, the neck of the flask was washed down with 2 ml. of  $\text{HCl}$  and the contents were digested vigorously until clear. After the solution cooled, 20 per cent  $\text{NaOH}$  was added until a permanent precipitate just formed. This was dissolved by a dropwise addition of 1 *N*  $\text{H}_2\text{SO}_4$ . Any brown discoloration that remained at the end of neutralization was cleared with a few drops of the sodium bisulfite reagent. The solution was then transferred to a 50-ml. volumetric flask and made to volume.

To determine the phosphorus in solutions prepared as above, an aliquot containing less than 50 gammas phosphorus in no more than 25 ml. of solution was pipetted into a 50-ml. volumetric flask. Quinaldine red was added, the acidity adjusted with 1 *N*  $\text{H}_2\text{SO}_4$ , and the volume made to 35 ml. with water. Five milliliters of the sodium bisulfite reagent was added and the flasks were heated in a boiling water bath for 40 minutes. Two milliliters of the dilute

molybdenum blue reagent was added and heating continued for 25 minutes. The cooled flasks were made to volume and the transmittancy was measured at 660  $m\mu$ .

#### TARTRATE DETERMINATION IN SODIUM PHOSPHATE EXTRACTS

Two methods for determining tartrate in 0.5 *M* sodium phosphate extracts were found to be satisfactory. One involved a dichromate oxidation, and the other a periodate oxidation (4). Because of its simplicity, the dichromate method was used for most determinations. The periodate method served as an occasional check.

A 10-ml. aliquot of the clarified extract was pipetted into a 250-ml. beaker and evaporated to dryness on a steam bath (to remove traces of alcohol). Ten milliliters of water was then added and 5 ml. potassium dichromate solution (4.9 gm. per liter) was accurately pipetted into the beaker followed by 10 ml. of 10 *N* sulfuric acid. The beaker was then covered and digested for 4 hours on the steam bath. At the end of the digestion period the cover glass was rinsed off and 50 ml. of water added to the beaker. To the cooled solution 5 ml. of 85 per cent phosphoric acid was added, and the excess dichromate was titrated with standard 0.05 *N* ferrous sulfate solution measured from a microburette using barium diphenylamine sulfonate as an indicator.

Reagent blanks were carried through the digestion and subsequent operations. Calculations were based upon the following formula:

$$\text{Millimols tartrate in aliquot} = \frac{(\text{ml. FeSO}_4\text{Blank} - \text{ml. FeSO}_4\text{Extract})}{10} \times \text{normality FeSO}_4$$

#### EFFECT OF CALCIUM PHOSPHATES ON DETERMINATION OF EXCHANGEABLE PHOSPHORUS

In considering the determination of the exchangeable phosphorus it is important to know whether there will be interference by phosphorus in forms other than the exchangeable. To test whether the presence of calcium phosphate will seriously affect the measurement of exchangeable phosphorus, a series of mixtures of calcium phosphates with purified quartz sand were prepared and subjected to a procedure for determining exchangeable phosphorus. Five grams of each of these mixtures, which contained 3 millimols of phosphorus per 100 gm., was pretreated with the sodium acetate solution and then extracted with the sodium arsenate solution by the same procedures as those applied to soils. The amounts of phosphorus dissolved by the two solutions were determined, and the results are given in table 3. These data show that the mono-calcium and dicalcium phosphates were completely dissolved by the pretreatment with sodium acetate, whereas the other forms were relatively insoluble. In no instance, however, did the sodium arsenate extract contain appreciable quantities of phosphorus.

The foregoing results, however, do not preclude the possibility that the calcium phosphate soluble in the sodium acetate pretreatment might be converted into exchangeable phosphorus during the pretreatment rather than be extracted from the soil. Consequently, 3 millimols of phosphorus as monocalcium phosphate was mixed with 100-gm. samples of Davidson soil, and these samples were then pretreated with sodium acetate followed by an extraction with sodium arsenate. The percentages of the added phosphorus removed by the sodium acetate pretreatment and the sodium arsenate extraction were determined. The results are given in table 4. Apparently it is possible for a soil having a high anion-exchange capacity to convert soluble phosphorus into exchangeable phosphorus. Acid soils, however, would rarely contain any very large amounts of monocalcium

TABLE 3

*Percentage of total phosphorus added to quartz sand removed by sodium acetate followed by a sodium arsenate extraction*

MATERIAL ADDED	PERCENTAGE OF TOTAL PHOSPHORUS REMOVED	
	Sodium acetate	Sodium arsenate
Curacao phosphate rock.....	11.1	0.0
Florida land pebble.....	2.3	0.0
Monocalcium phosphate.....	100.5	0.0
Dicalcium phosphate.....	94.6	0.6
Tricalcium phosphate.....	27.7	0.0
Hydroxylapatite.....	12.4	0.0

TABLE 4

*Percentage of total phosphorus from monocalcium phosphate added to soils removed by sodium-acetate followed by sodium arsenate extraction*

SOIL	ANION-EXCHANGE CAPACITY  <i>millimols/100 gm.</i>	PERCENTAGE OF TOTAL PHOSPHORUS REMOVED	
		Sodium acetate	Sodium arsenate
Atwood.....	3.7	98.2	0.0
Davidson.....	14	68.4	23.3

phosphate, and if the pretreatment is made rapidly, it is not likely that significant amounts of exchangeable phosphorus will be formed.

#### SUMMARY

This paper embraces the essential features of methods for determining the anion-exchange capacity, the exchangeable phosphorus, and the anion reactions of soils. Procedures are given for extracting exchangeable anions and for preparing soils saturated with anions. Analytical methods are outlined for the determination of phosphates in extracts containing 0.5 *M* concentrations of arsenate, fluoride, citrate, and tartrate ions. Also, methods are given for the determination of arsenates and tartrates in 0.5 *M* phosphate extracts.

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# ANION EXCHANGE IN SOILS: III. APPLICABILITY TO PROBLEMS OF SOIL FERTILITY

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The concepts of anion exchange in soils (6) afford the opportunity to consider a readily definable fraction of the soil phosphorus in relation to problems of soil fertility. There is little evidence to show that the common methods for evaluating the availability of soil phosphorus give more than a relative index of the phosphorus fertility status. The phosphorus extracted by these methods is frequently derived by partially dissolving several of the phosphorus fractions contained in soils. An appraisal of a definite fraction of the soil phosphorus could possibly lead to a better interpretation of the values obtained by the common methods of determining available phosphorus, show overall changes occurring from cropping and farm management practices, and allow interpretation of the influence of soil composition and environmental factors on the availability of this fraction to crops.

Over a hundred soil samples have been examined in this laboratory relative to their anion-exchange capacity and exchangeable phosphorus content. Most of the soil samples examined were collected in conjunction with a previously reported study (9). They were acid, highly fertilized soils from potato farms in the Atlantic and Gulf Coast states. It is the purpose of this paper to examine these data from the standpoint of their applicability to soil fertility problems.

## CORRELATION OF ANION-EXCHANGE DATA AND TRUOG PHOSPHORUS VALUES

The Truog method (13) for determining the readily available phosphorus has been found to be satisfactory for evaluating the phosphorus fertility of many types of soils. Findings relative to possible correlations between the anion exchange and Truog available phosphorus data are not necessarily criteria for evaluating the anion-exchange data. On the other hand, if such correlations exist they might well serve as an aid when Truog phosphorus values are used to evaluate the fertility status and the changes in this status which may occur.

The anion-exchange capacity, exchangeable phosphorus, and Truog phosphorus [modified (10)] data were available on 103 soil samples collected from potato fields in Maine, New York, New Jersey, Maryland, Virginia, North Carolina, and Alabama. These soils all had pH values of less than 5.5 and had been used to grow at least five crops of potatoes. A summary of the statistical analysis of the data from these samples is given in tables 1 and 2. The results of this analysis indicate that there are significant correlations between the Truog phosphorus values and the exchangeable phosphorus, the anion-exchange capac-

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ity, and the degree of saturation. The Truog phosphorus is directly related to the exchangeable phosphorus and the degree of saturation but inversely related to anion-exchange capacity.

The partial regression coefficients of Truog phosphorus on exchangeable phosphorus and anion-exchange capacity are both significant to a much higher degree than are the simple regressions discussed above. For example, the Truog phosphorus is correlated with the anion-exchange capacity to a much higher degree of significance when corrections are made for the differences in exchangeable phosphorus than when these adjustments are not made. Thus, the Truog phos-

TABLE 1

*Analysis of data for 103 soils samples collected on potato farms in eastern United States*

DESCRIPTION	MEAN	STANDARD DEVIATION	MAXIMUM	MINIMUM
Exchangeable phosphorus.....millimols/100 gm.	1.58	0.564	3.1	0.53
Anion-exchange capacity.....millimols/100 gm.	5.45	4.14	17.2	1.2
Degree of saturation.....per cent	43.7	27.02	117.0	6.9
Modified Truog phosphorus...lbs.P/2,000,000 lbs.	245.5	142.6	804.0	25.0

TABLE 2

*Regression coefficients of modified Truog phosphorus values on exchangeable phosphorus, anion-exchange capacity, and degree of saturation*

REGRESSION COEFFICIENT OF MODIFIED TRUOG PHOSPHORUS VALUE ON:			t VALUES OF REGRESSION COEFFICIENTS:		
Exchangeable phosphorus	Anion-exchange capacity	Degree of saturation	Exchangeable phosphorus	Anion-exchange capacity	Degree of saturation
123.17	-13.73	3.31	5.65	4.30	8.08
PARTIAL REGRESSION COEFFICIENTS					
200.4	-25.1		12.7	11.0	

phorus can be predicted with a considerable degree of confidence from the following regression equation:

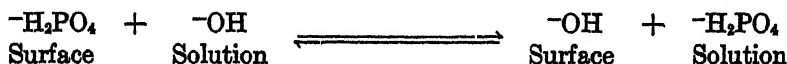
$$y = 200.4x - 25.1z + 65.9 \quad (1)$$

where  $y$  = Truog phosphorus (pounds P per 2,000,000 pounds soil),  $x$  = exchangeable phosphorus (millimols P per 100 gm.), and  $z$  = anion exchange capacity (millimols P per 100 gm.). It should be borne in mind, however, that this equation was derived from data on soils having certain characteristics. In particular, all the soils were very acid ( $< \text{pH } 5.5$ ) and probably contained little or no soluble phosphorus with the exception of the exchangeable phosphorus.

## ANION EXCHANGE IN RELATION TO PHOSPHORUS AVAILABILITY

There is no reason to believe that the exchangeable phosphorus values for a group of unrelated soils would be directly related to their phosphorus fertility. In the first place, soils may or may not have, in addition to the exchangeable phosphorus, appreciable amounts of other forms of phosphorus available to plants. In order that the exchangeable phosphorus be available to plants, one of two conditions must prevail; namely, that plants utilize exchangeable phosphorus by contact feeding, or that the exchangeable phosphorus supplies the soil solution with phosphate ions. Studies by Dean and Rubins (5) and Overstreet (8) tend to minimize the importance of contact feeding as a means by which plants may utilize the phosphorus associated with the clay surfaces.

When an acid soil containing only exchangeable phosphorus is suspended in water, the equilibrium which will be established between the phosphorus associated with the solid phase and that in solution may be represented by the following equation:



Equilibrium constants calculated from

$$K = \frac{C_{\text{OH}(\text{solution})} \times C_{\text{H}_2\text{PO}_4(\text{surface})}}{C_{\text{OH}(\text{surface})} \times C_{\text{H}_2\text{PO}_4(\text{solution})}} \quad (2)$$

have been found to approximate a constant (5). The  $C_{\text{H}_2\text{PO}_4(\text{surface})}$  and  $[C_{\text{H}_2\text{PO}_4(\text{surface})} + C_{\text{OH}(\text{surface})}]$  may be taken to be the exchangeable phosphorus and the anion-exchange capacity of soils, respectively. In other words, the composition of the soil solution in respect to phosphate ions and to the rate at which this concentration is maintained is a function of the pH, exchangeable phosphorus, and anion-exchange capacity. The presumption, then, is that these are the factors which influence the availability of exchangeable phosphorus. This also offers one explanation for the frequent observation that liming increases the availability of phosphates in soils.

Other things being equal, it would be expected that the phosphorus fertility would be increased by increasing the degree of saturation in respect to phosphorus. When a group of miscellaneous soils are considered, however, the degree of saturation could not be expected to give more than a general index of the phosphorus fertility status of each.

It may be of interest to examine on theoretical grounds the phosphorus fertility status of two acid soils which have only exchangeable phosphorus, the same pH and Truog phosphorus values, but have different anion-exchange capacities. If it is assumed that these hypothetical soils have Truog phosphorus values of 100 pounds per acre and anion-exchange capacities of 3 and 10 millimols per 100 gm., then by calculation from equation (1) the exchangeable phosphorus contents of these soils will be 0.55 and 1.47 millimols per 100 gm. Thus, one soil has a much greater potential supply of available phosphorus than the other. Will these two soils supply phosphorus to plants at the same rate? The potential



rate of supply to plants may depend upon the concentration of the soil solution, and the amount of soil solution per unit volume of soil.

Since the soils under consideration have the same pH, equation (2) may be rewritten as follows:

$$C_{\text{H}_2\text{PO}_4(\text{solution})} = r \frac{C_{\text{H}_2\text{PO}_2(\text{surface})}}{C_{\text{OH}(\text{surface})}} \quad (3)$$

where  $r = \frac{C_{\text{OH}(\text{solution})}}{K}$ . It would then follow that the relative concentration of the soil solution for the soil having an anion-exchange capacity of 3 millimols per 100 gm. would be  $r \times \frac{0.55}{3-0.55}$  or  $0.22 r$ . Likewise the soil with the anion-exchange capacity of 10 would have a relative soil solution concentration of  $0.17 r$ , provided the values of  $K$  for the two soils are equal.

It has been shown (6), when considering soils of the same series, that the anion-exchange capacity increases with increasing clay content. A review of the data available on anion-exchange capacity showed that soils having anion-exchange capacities of about 3 are sands or sandy loams, whereas soils with anion-exchange capacities of about 10 are silt or clay loams. Thus it is probable that a plant growing in the soil having an anion-exchange capacity of 10 would have in the order of 50 to 100 per cent more soil solution at only a slightly lower phosphorus concentration to feed from than a plant growing in the soil having the anion-exchange capacity of 3. A unit volume of soil will have a greater number of phosphate ions in solution at a given time in the case of the soil having the higher anion-exchange capacity.

#### ACCUMULATION OF PHOSPHORUS IN SOILS

For the purpose of discussion, the phosphorus of soils will be classified as follows:

1. Exchangeable phosphorus.
2. Salts of divalent bases, that is, the calcium phosphates.
3. Organic phosphorus compounds.
4. Inert inorganic phosphorus compounds.

This is essentially the same classification as that previously given by Dean (4) except the fraction termed "inorganic alkali-soluble" has in the light of more recent work been renamed "exchangeable phosphorus." The method used for determining the inorganic alkali-soluble phosphorus was, in actuality, measuring the exchangeable phosphorus.

The two inorganic soil phosphorus fractions which are altered to the greatest degree by cropping, fertilization, and changes in soil properties (pH and exchangeable bases) are the exchangeable and the divalent-base fractions. These two fractions differ in their chemical properties. The phosphorus compounds which are salts of the divalent bases are readily soluble in dilute solutions of the strong mineral acids but are quite insoluble in alkalis, especially in the presence of excesses of divalent bases. The exchangeable phosphorus, on the other hand,

readily enters solution in the presence of hydroxyl ions. Since it is the tendency of weathering processes to convert matter into stable forms, it would be expected that acid soils would contain more exchangeable phosphorus than phosphorus in the form of salts of divalent bases, and in neutral or alkaline soils reverse conditions should prevail. Studies by Dean (3, 4) have shown the distribution of phosphorus applied to soils under laboratory conditions and as fertilizers in

TABLE 3

*Anion-exchange, modified Truog, and total phosphorus data on twelve representative soils*

SOIL NO.	DESCRIPTION OF SOILS	Exchange- able phos- phorus	Anion- exchange capacity	Degree of satu- ration	Modified Truog values	Total phos- phorus	pH
		mmols./100 gm.	mmols./100 gm.	per cent	mmols./100 gm.	mmols./100 gm.	
45348	Keyport sandy loam, Va.; 40 potato crops were grown in 50 years	1.8	1.8	100.0	0.81	3.3	5.1
45350	Keyport sandy loam, Va.; virgin area adjacent to sample 45348	0.24	1.6	15.0	0.05	0.6	4.6
E1171	Sassafras loamy sand, N. J.; cultivated trucking area for over 60 years	1.4	1.3	110.0	0.50	2.2	5.1
E1753	Collington loam, N. J.; continuous potatoes for 25 years	2.0	6.1	33.0	0.59	5.6	5.7
E1568	Sable silty clay, Ill.; from permanent sod on Minonk Experiment Field	0.41	5.8	7.1	0.06	2.1	6.3
C4745	Brookston clay, Ohio; response to phosphorus fertilizer doubtful	0.54	4.7	11.0	0.33	3.1	6.4
C4746	Wooster silt loam, Ohio; response to phosphorus fertilizer high	0.23	3.7	6.2	0.01	1.1	6.9
C4740	Cecil sandy clay loam, Ga.; response to phosphorus fertilizer doubtful	0.88	4.1	21.0	0.17	2.2	4.9
E915	Caribou loam, Me.; permanent fertility plots, 3-year rotation 4-0-8 plot	0.83	9.6	8.6	0.04	2.6	5.2
E959	Caribou loam, Me.; permanent fertility plots, 3-year rotation 4-8-8 plots	1.2	9.6	13.0	0.11	3.1	5.3
E787	Davidson clay loam, Va.; uncultivated area, Orange Co. sub-station	0.53	10.0	5.3	0.03	2.5	6.0
E1824	Hawaiian clay soil	1.7	30.0	5.7	<0.01	10.0	5.5

permanent field experiments. In acid soils most of the applied phosphorus occurs as exchangeable phosphorus, whereas in slightly alkaline soils containing a small amount of calcium carbonate the phosphorus occurs mostly as salts of the divalent bases. Apparently the transition zone is in the neighborhood of pH 6. Presumably then, the exchangeable phosphorus fraction is of most importance in those soils of pH less than 6.

The accumulation of phosphorus as exchangeable phosphorus in acid potato

soils has been previously reported (9), and therefore further discussions of this will be limited. Anion-exchange data and total and Truog phosphorus values, for a series of selected soil samples are given in table 3 to illustrate the scope involved. The anion-exchange data were obtained by saturating soils with arsenate and displacing the adsorbed arsenate with phosphate. The phosphate contained in the arsenate extracting solutions was considered to be the exchangeable phosphorus. [For a detailed description of methods, see previous paper (12).]

The exchangeable phosphorus in acid soils varies from the low amounts found in some virgin soils to the very high amounts found in some of the heavily fertilized soils. It is not unusual to find exchangeable phosphorus in excess of 2000 pounds per acre in the highly fertilized soils of the eastern seaboard. In some instances as much as 60 per cent of their phosphorus is in the exchangeable

TABLE 4  
*Concentrations of phosphorus in percolates passing through 8-cm. columns of soils*  
Concentrations in p.p.m. P

ORIGINAL SOLUTION	1ST PERCOLATE	2ND PERCOLATE	3RD PERCOLATE	4TH PERCOLATE
<i>Bertie Soil (100 per cent saturated)</i>				
0	3.9	6.0	6.4	4.6
2.5	4.2	5.6	7.2	6.6
5	4.0	6.0	8.1	8.4
10	4.2	7.2	10.1	11.1
<i>Sassafras Soil (50 per cent saturated)</i>				
0	1.5	2.2	2.5	2.8
2.5	1.6	2.2	2.9	3.1
5	1.6	2.2	3.0	3.3
10	1.6	2.2	3.2	4.1

form. In most instances the Truog phosphorus values were relatively low as compared with exchangeable and total phosphorus. However, some neutral or slightly calcareous soils having low amounts of exchangeable phosphorus will frequently give relatively high Truog values (4).

The degree of saturation or the percentage of the anion-exchange capacity which is saturated with phosphorus has been found to vary from about 5 to over 100. The reason for finding soils with degrees of saturation in excess of 100 per cent is that the arsenate method was used in determining the anion-exchange capacity, and many soils are capable of adsorbing considerably more phosphate than arsenate (6).

#### LEACHING OF PHOSPHORUS

Comparisons of the distribution of total and exchangeable phosphorus in soil profiles from heavily fertilized fields and adjacent virgin areas have shown

an increase in the phosphorus contents of both surface and subsoils (7, 9). This downward movement of phosphorus could be caused either by leaching or by a mechanical process. In this regard it became of interest to consider the leaching of phosphorus in soils which have become saturated to a high degree with phosphorus.

The exchangeable phosphorus of soils tends to establish an equilibrium with the soil solution. In other words, if a soil is bathed in a solution containing a lower concentration of phosphate ions than its equilibrium concentration, the soil will impart phosphate ions to the solution, whereas if the bathing solution is at a higher concentration, the reverse takes place. With most soils the equilibrium concentration is very low, less than 0.1 p.p.m. P, and there is little tendency for phosphorus to leach. Some of the intensively fertilized sandy soils of the eastern seaboard having low anion capacities have become saturated with phosphorus to such a degree, however, that the equilibrium concentration is now greater than 1 p.p.m., and leaching of phosphorus in these soils is not improbable.

A laboratory leaching experiment using columns of two highly saturated soils was undertaken to demonstrate the leaching of phosphorus. Fifty-gram soil samples were packed into leaching tubes making columns of soil 2.5 cm. in diameter and about 8 cm. in height. These columns of soil were slowly leached with successive 100-ml. portions of  $\text{KH}_2\text{PO}_4$  solutions containing 2.5, 5, and 10 p.p.m. of P. The concentration of phosphorus in each of the leachates was then determined. The results are given in table 4. These data indicate a tendency for the leachates of a given soil to attain a definite concentration irrespective of the original concentration of the leachate. It is also evident from these data that the equilibrium concentrations of these highly saturated soils are sufficient to allow a considerable downward movement of phosphorus into the lower horizons.

#### DISCUSSION

Several investigators have suggested methods of fractionating the soil phosphorus (1, 2, 4) for the purpose of giving a more refined review of the fertility status than offered by the conventional methods. Several drawbacks have been encountered. Clear-cut and complete differentiation of known chemical entities has not always been attained, thus making interpretation of the data uncertain. The exchangeable phosphorus is a fraction which may be separated with little interference from the other fractions, and its chemical properties in relation to soil properties in general may be readily investigated. In only a relatively small group of soils, however, may the exchangeable phosphorus be considered the only important potential phosphorus supply. Nor are the equilibria which exist between the exchangeable phosphorus and other forms completely understood.

The magnitude of the amounts of phosphorus which comprise fractions such as the exchangeable phosphorus are great compared with the requirements of normal crops or the amounts obtained by the usual methods [such as listed by

Rubins and Dean (11)] of determining available phosphorus. This has tended to cause confusion. Perhaps the available phosphorus values for acid soils containing a predominance of exchangeable phosphorus more nearly approximate an intensity rather than a quantity factor. For example, in the case of an acid soil containing only exchangeable phosphorus, a rough analogy might be drawn between the exchangeable phosphorus and the exchangeable hydrogen as quantity factors and the Truog phosphorus and the pH as intensity factors. Should not both a quantity and an intensity factor be considered in the evaluation of the phosphorus fertility status of soils?

To reiterate, this paper has been concerned with the applicability of the concepts of anion exchange in the evaluation of the phosphorus fertility status of soils. In acid soils, phosphorus tends to accumulate as an exchangeable anion. The amounts of exchangeable phosphorus which acid soils contain are not, however, necessarily a reliable index of the fertility status of these soils, since the anion-exchange capacity, the pH, and the amounts of other forms of phosphorus are also contributing factors. Partial regression coefficients of Truog phosphorus values of very acid soils on exchangeable phosphorus and anion-exchange capacity were both highly significant. The anion-exchange data are probably better applied as complementary data than as a substitute for the conventional methods of determining available phosphorus.

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# FIXATION OF POTASSIUM IN RELATION TO EXCHANGE CAPACITY OF SOILS: V. MECHANISM OF FIXATION<sup>1</sup>

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In the foregoing papers of this series (21, 25) K fixation was discussed first from the point of view of its release to soluble forms and then with regard to its relationship to the exchange complex. Comparisons between  $\text{NH}_4$  and K fixation led to the conclusion that the fixing mechanism is the same for both ions.

The work described intimated also that the fixing mechanism was very similar, or the same, for different materials. This subject is discussed in the present paper.

## DIFFERENTIAL FIXATION OF K BY VARIOUS MINERALS

Many theories have been advanced in an attempt to elucidate the mechanism of the fixation process. Volk (32) suggested that K reacts with "so-called" silicates to form difficulty soluble muscovite. According to Gorbunov (11), K is fixed in soil gels by an occlusion process which depends primarily on the electrokinetic condition of the soil. Chaminade and Drouineau (4) advanced the view that fixation is caused by the migration of K from the surface of a colloid into the interior of the crystal, which is coated by the colloid. The thesis that K is fixed between the layers of the expanding and contracting c-axis of layer lattice minerals was discussed by Truog and Jones (31), Page (30), and Kolodny.<sup>3</sup> Kolodny showed that when montmorillonite layers are collapsed by heating to temperatures of about  $550^\circ\text{C}$ ., the ability of montmorillonite to fix K diminished to the vanishing point. In general, he found that with the decreasing ability of montmorillonite to swell reversibly, there was a decrease in the ability of the mineral to fix K.

The capacity to fix K varies with the minerals. Kaolinite, albite, and orthoclase fix very little, if any. This condition is reflected in soils, for a soil like the Cecil series which contains large quantities of kaolinite (1, 28) fixes only very small amounts of K<sup>4</sup>. Those minerals which do fix K are very similar in at least one respect, they all have layer lattice structures. Montmorillonite, which is known for its ability to fix K, is a leading example of this type of mineral. Chaminade (3) and Levine<sup>4</sup> have shown that glauconite, also a layer-structure min-

<sup>1</sup> Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers University, department of soils.

<sup>2</sup> Temporarily withdrawn; resubmitted December 16, 1946.

<sup>3</sup> Kolodny, L. Mechanism of potassium fixation in soils and the availability of fixed potassium to plants. 1938. [Unpublished doctor's thesis. Copy on file, Rutgers University Library, New Brunswick, N. J.]

<sup>4</sup> Levine, A. K. Relation of potassium fixation to the exchange capacity of soils. 1939. [Unpublished master's thesis. Copy on file, Rutgers University Library, New Brunswick, N. J.]

eral (15), fixes large quantities of K. Moscovite is another mineral of this general class, and Volk (32) has shown that when this mineral does not have its full complement of K it will fix that element. In papers I and II (21) of this series it was shown that when K is removed from sericite that layer mineral will fix K. Pyrophyllite is also a layer mineral (13); as will be shown below, this mineral can be made to fix K. These remarks are also true for a large group of clay minerals, the hydrous micas.

Many of these layer minerals and mixed layer minerals are found in the soil. Many investigators (6, 7, 17, 22, 24, 28) have reported montmorillonite to be a constituent of soil colloids, particularly those formed under conditions of high pH. Glauconite is found in soils formed on greensand. Micas and hydrous micas have been observed in soil colloids for some time and have been thoroughly investigated by Grim, Bray, and Bradley (12) and by Hofmann and his co-workers (20). Illite is also a hydrous mica. The occurrence of layer and mixed layer minerals in soil colloids leads to the belief that it is these minerals that fix the K in soils.

#### EXPERIMENTS WITH PYROPHYLLITE

The basic or fundamental unit of which bentonite or montmorillonite is built is the pyrophyllite unit (14). According to Volk (34), pyrophyllite itself fixes no K. Since bentonite fixes very large quantities of K, and since pyrophyllite is a member of the same class of minerals, it was decided to investigate the reason no fixation was found with pyrophyllite.

The pyrophyllite used in these experiments<sup>5</sup> contained less than 0.02 per cent total K.

Duplicate 5-gm. samples of 325-mesh pyrophyllite were treated with 15.00 ml. of KCl (1 ml. = 5.03 mgm. K). The systems were alternately wetted and dried several times at 105°C., to induce K fixation, but no measurable fixation took place. A determination of the exchange capacity at pH 7 showed that the pyrophyllite contained only 0.011 m.e. of exchange positions per gram. Since K cannot be fixed unless it is first present in exchangeable form, the extremely low exchange capacity of the pyrophyllite might well be the reason that no fixation was observed.

A further attack was suggested by the work of Kelley, Dore, and Brown (22) and Kelley and Jenny (23). These investigators noted that the exchange capacity of many minerals can be markedly increased by vigorous grinding, as in a ball mill. In general, the longer the period of grinding, the greater the increase in the exchange capacity. Since the exchange capacity can be raised in this way, the influence of grinding pyrophyllite on its ability to fix K was investigated.

Pyrophyllite of 325-mesh fineness was ground in a ball mill for 120 hours. By this treatment the exchange capacity at pH 7 was increased to 0.156 m.e. per gram, or about fifteen times its original value. Duplicate 5-gm. samples of the

<sup>5</sup> Furnished by Carolina Pyrophyllite Company from their Staley, North Carolina, plant.

ground pyrophyllite were treated identically as above. In this instance, however, fixation was about 2.5 mgm. per gram.

Besides justifying the prediction that pyrophyllite, as a mineral of the layer-lattice type, will fix K, the result of the experiment also underlines the essential nature of the exchange complex with regard to fixation. When no K was able to enter the exchange complex, none was fixed; fixation had to await some method for getting K into the exchange complex. This, of course, also explains why Volk was unable to fix K in pyrophyllite.

For another experiment, the pyrophyllite which had already been ground 120 hours was ground 48 hours more. The exchange capacity was determined to be 0.379 m.e. per gram. Five grams of this was treated with a solution of KCl and the fixing procedure applied immediately after. The work was done in duplicate. No fixation could be detected.

Why the ground pyrophyllite should fix K in one case and not in another even when the exchange capacity was further increased was not immediately apparent. Work by Kunin<sup>6</sup> clarified the situation. Working with the very same sample of pyrophyllite (ground 168 hours), Kunin found that equilibrium between the pyrophyllite and exchanging ions was not established except after contact over an extended period of time. Though an appreciable quantity of cation (Ba in this case) entered into exchange almost immediately, much larger amounts were observed to enter after the system stood for a few days. Evidently the initial exchange was on the external surface (26), whereas the exchange that took place more slowly was between the layers.<sup>7</sup> Cernescu (2) has shown that zeolites and permutites require a long time to come to exchange equilibrium with a solution of cations. Because of the very fine "pores" in the structure of those materials, the cations have difficulty in reaching exchange positions. The very narrow spacing between the pyrophyllite layers in the lattice probably offers a similar difficulty. With bentonite, where the interlayer distances are very much larger, equilibrium was observed to occur virtually instantaneously. Evidently, in the first case where fixation was noted, the KCl was allowed to remain in contact with the pyrophyllite for a considerable time; thus K ions were permitted to enter between the layers where they were in position for fixation. Where no fixation was realized, the K was not given sufficient time to enter between the layers, since immediately on application of the K solution the system was put in the oven to dry.

To check the postulate just advanced, a further experiment was undertaken. A sample of pyrophyllite was kept in contact with K solution for a long time

<sup>6</sup> Kunin, R. Unpublished data.

<sup>7</sup> An anonymous reviewer of this paper notes the following: "The changes caused by dry grinding are more deep-seated even than Kelley and Jenny believed. The whole lattice is destroyed if the grinding is sufficiently prolonged and it is no longer possible to regard the mineral as pyrophyllite or as montmorillonite. This is shown in three ways. First, by an assumption of an amorphous x-ray pattern in place of the crystalline; second, by changes in the optical properties; third, by changes in the chemical properties. See *Jour. Phys. Chem.* 41: 935-942 (1937)" [paper by C. E. Marshall, entitled "Colloidal properties of the clays as related to their crystal structure"].



before the system was dried. At the conclusion of the experiment, it was found that K had been fixed. Besides verifying the above hypothesis, this result has important implications regarding the mechanism of fixation.

#### EXPERIMENTS WITH BENTONITE

Another series of experiments designed to focus attention on the mechanism of the fixing process were performed with bentonite. Hydrogen bentonite of exchange capacity 0.79 m.e. per gram was ground in a ball mill for 60 hours. The exchange capacity increased to 1.25 m.e. per gram.

A 2.000-gm. sample of the ground bentonite and a 3.125-gm. sample of the unground mineral were treated with 20.00 ml. of 0.1246 *N* KCl. The 2.000 gm. of ground bentonite had an exchange capacity equal to that of the 3.125 gm. of unground material, and both samples were symmetrical with the quantity of K added. Also 3.125 gm. of ground bentonite was treated with 20.00 ml. of 0.1246 *N* KCl. The systems were treated to cause fixation (at 105°C.), and the quantity of K fixed was determined. The work was done in duplicate. Table 18 gives the data.

The samples having equivalence of exchange capacity were found to fix almost equal amounts of K. Offhand, from the theory developed above, this is to be looked for. Data in subsequent tables, however, indicate that the closeness of the experimental results may merely be coincidental.

A further noteworthy feature of table 18 is the small amount of fixation by the 3.125-gm. ground sample. This sample had a much larger exchange capacity than either of the others, and certainly more K entered its exchange complex (see tables 19 and 20). In the previous experiments, the greater the quantity of K in the exchange complex, the larger the fixation. Why the difference in this case? For one thing, in the previous experiments the exchange complex was not altered: only the amount of K which was allowed to enter the complex was varied. In the investigation described above, the exchange complex itself was changed, and in the process of changing, many different attributes were imparted to the exchange complex. Thus, the type of exchange which was added to the original exchange may be different. For instance, a certain portion of the original exchange was between the layers of the crystal lattice (8, 9, 10, 19, 23, 26, 29). When the mineral is ground, the amount of exchange between the layers is negligibly altered in comparison with exchange on other parts of the crystal; that is, the exchange capacity is increased by breaking across the layers of minerals, thus leaving broken bonds on the edges of the Si-O planes (20) or exposing O-H groups (23). If, as is postulated, K is fixed between the layers, then increasing the exchange capacity with types of exchange that do not fix K merely diverts K from being fixed.

If more K were able to enter the complex in an experiment similar to the foregoing, some of the results from table 18 should be changed. Since the ions in the exchange complex at the outset are primarily hydrogen, the end sought could be attained by using a salt such as potassium acetate. Under such con-

ditions more K will enter, since the acetate removes the H ions to form the slightly dissociated acetic acid.

For the next phase of this work, larger samples were chosen so that larger amounts of K would be fixed: 3.112 gm. of ground hydrogen bentonite, 4.924 gm. of unground bentonite, and 4.924 gm. of ground bentonite were treated

TABLE 18  
*Effect of grinding H-bentonite on fixation of K added as KCl*

DESCRIPTION	K FIXED*	
	mgm.	m.e.
3.125 gm.; unground	8.7	0.22
2.000 gm.; ground	7.6	0.19
3.125 gm.; ground	3.4	0.09

\* 2.49 m.e. K added originally

TABLE 19  
*Effect of grinding H-bentonite on fixation of K added as aqueous AcOK*

DESCRIPTION	K RECOVERED*		TOTAL EXCHANGE CAPACITY	AMOUNT OF K WHICH ENTERED EXCHANGE COMPLEX*	K FIXED
	H <sub>2</sub> O-soluble	HCl-soluble			
	m.e.	m.e.	m.e.	m.e.	m.e.
4.924 gm.; unground	1.35	2.10	3.89	2.54	0.44
3.112 gm.; ground	1.10	2.65	3.89	2.79	0.14
4.924 gm.; ground	0.60	2.75	6.13	3.29	0.54

\* 3.89 m.e. K added originally.

TABLE 20  
*Effect of grinding H-bentonite on fixation of K added as alcoholic AcOK*

DESCRIPTION	K RECOVERED*		TOTAL EXCHANGE CAPACITY	AMOUNT OF K WHICH ENTERED EXCHANGE COMPLEX*	K FIXED
	Alcohol-soluble	HCl-soluble			
	m.e.	m.e.	m.e.	m.e.	m.e.
4.924 gm.; unground	0.68	2.37	3.89	3.21	0.84
3.112 gm.; ground	0.45	2.81	3.89	3.43	0.63
4.924 gm.; ground	0.15	2.58	6.13	3.74	1.16

\* 3.89 m.e. K added originally.

respectively with 3.89 m.e. of potassium acetate. This quantity of K was symmetrical with the first two samples. The systems were fixed at 105°C. and then extracted first with water then with 0.05 N HCl. Table 19 lists the results.

The effect of the acetate radical is readily discernible. Large quantities of K are seen to have entered the exchange complex, resulting in a relative degree of K saturation sufficiently great to allow large fixation. Although large quantities

of K entered the exchange complex of the 3.112-gm. ground sample, fixation in this instance was less than with the 4.924-gm. unground sample where less K entered the exchange complex. This is readily explained on the basis of the new type of exchange created during grinding; a type of exchange which does not permit K to revert to the nonexchangeable state. In other words, for an exchange position to be effective in bringing about K fixation it must be situated between the layers perpendicular to the (001) plane. Though the exchange capacities of the 3.112-gm. ground sample and the 4.924-gm. unground sample are equal, the latter has more interlayer exchange and so is capable of greater K fixation.

It may be argued, however, that the quantity of interlayer surface is virtually the same in the ground and the unground sample of the same weight, since the magnitude of the interlayer surface is a function of the weight of the mineral. If this is so, why is there greater fixation in the case of the ground system? Though K is fixed only when exchanged on interlayer positions, not all the interlayer potential exchange positions are accessible for exchange. When the mineral is ground there is much breaking parallel to the c-axis. This breaking exposes "new" (previously unexposed) interlayer surface (and interlayer exchange positions) to exchanging cations. With the increase in the portion of layer surface available for exchange, an increase in potassium fixation is to be expected. And that is actually what happens.

#### EXPERIMENTS WITH ALCOHOLIC SOLUTIONS

The experiments reported in table 19 were repeated, with alcoholic potassium acetate, alcohol as the initial extracting agent of alcoholic potassium acetate for the aqueous solution medium after fixation, and the substitution of 0.05 *N* alcoholic solution of HCl for the aqueous solution. Results appear in table 20.

The data of table 20 compare very well with those of table 19. Of course, there is an increase in the quantity of K fixed, but this was expected. The increase in fixation over the previous experiment results in part from the greater ability of K to penetrate interlayer spaces when in alcoholic solution than in water. Some work by Wiegner (34) indicates that this is so. It is very interesting, too, to note that the 4.924-gm. ground sample took virtually all the K—about 96 per cent—into the exchange complex. This is, of course, also due to the greater ease with which K enters the exchange complex when in alcoholic medium.

The explanation of the data in table 20 follows the same lines employed in table 19. The larger fixations merely serve to emphasize the foregoing remarks.

#### GENERAL DISCUSSION ON LAYER MINERALS

That the alkali content of many micaceous and other layer minerals is often considerably below that which they should contain theoretically has been pointed out by Gruner (15). The same thing has been pointed out for hydrous micas by Hendricks and Alexander (18). According to Gruner, not all the K positions in

the interlayer lattice structure are occupied. The number of "holes" depends, probably, on the number of Al and perhaps  $\text{Fe}^{+++}$  replacing Si. Theoretically for every Al or  $\text{Fe}^{+++}$  in the  $(\text{SiAl})_4\text{O}_{10}$  tetrahedral layer there should be a K ion in the structure. Compared with the work of Denison, Fry, and Gile (7), who found that weathering of micaceous minerals in the soil was accompanied by a decrease in the K content and an increase in the Al content, the hypothesis of Gruner becomes very applicable to the fixation phenomenon with K. Evidently what takes place is that when the K is introduced into the system, some of it is exchanged on positions where "holes" exist. On wetting and drying of the mineral, the K is retained and becomes part of its structure. It is quite possible that an appreciable number of these "holes" are created during previous weathering processes, as noted above. In other cases "holes" may exist because of a deficiency of K available when the mineral was originally formed.

Gruner (16) treated vermiculite first with hydrogen peroxide to exfoliate it, and then with  $\text{NH}_4\text{OH}$ . After removal of the excess  $\text{NH}_4\text{OH}$  with water, the system was dried at  $50^\circ\text{C}$ . When the sample was x-rayed, Gruner noted that some of the vermiculite had been converted to ammonium mica. The similarity of this process to  $\text{NH}_4$  fixation as described (21) is clear at once, and only serves to re-emphasize that when fixation occurs, the fixed ion (K or  $\text{NH}_4$ ) becomes part of the crystal structure of the mineral.

After he had caused the ammonium mica to be formed, Gruner noticed a very decided shrinking in the (001) plane, as compared to that spacing before the experiment. In this connection, Nagelschmidt's observations (28) on bentonite are interesting. He reported that when bentonite is saturated with Ca or Mg the basal spacing (001) is 15 Å., but if K is the exchangeable ion, the (001) spacing is only 12 Å. This is interpreted as implying that fixation results in a decrease in the (001) spacing.

A visual observation by Mattson (27) fits in with the conclusions drawn from the x-ray work of Gruner and Nagelschmidt as reported above. Mattson found that Sharkey and Norfolk colloids, when saturated with Na or Li and then dried, readily imbibed water subsequently added to them, and formed voluminous gels. When the colloids were saturated with K, however, and then dried, there was no tendency to swell on wetting. On the other hand if the K-saturated colloids were not dried they swelled considerably. Though Mattson did not explain the results, they are clearly explicable on the basis of K fixation. In the Na- and Li-saturated colloids there was no fixation, and hence drying did not markedly affect their swelling properties. The K-saturated colloid when not dried exhibited no fixation either; hence, there was no effect on its swelling properties. When the K-saturated colloid was dried, however, fixation and a consequent shrinking along the c-axis occurred, seriously inhibiting swelling.

A decrease in the basal spacing should be reflected in the specific gravity of the mineral. That is, because of the more compact structure, an increase in specific gravity should result. Some work with Kunin has shown this to be the case. The specific gravity of K-fixed bentonite was compared with that of nonfixed

bentonite. Both samples had been treated alike in all details, save that one was fixed with K, and the other was not. The nonfixed bentonite was found to float on the surface of a liquid of specific gravity 2.30, whereas the sample in which K had been fixed sank to the bottom. Closer work on the K-fixed bentonite showed that its specific gravity was between 2.35 and 2.40, which seems to testify that fixed K becomes part of the crystal structure of the mineral.

N. J. Volk (33) concluded that K was fixed as muscovite, and G. W. Volk (32) ran an experiment designed to look into this conclusion. Several different samples of muscovite containing from 9.3 to 10.8 per cent K, the theoretical being 11.8 per cent, were treated with aqueous KCl and the fixing procedure was applied at 70°C. Volk (32) found that the muscovites more deficient in potash fixed more K than the muscovites which had more nearly their theoretical complement of K. Although this does not justify the conclusion that K is fixed as muscovite for instances other than this particular one, the results fit in with the theory developed above.

Chaminade and Drouineau (4) found that prolonged grinding released almost all the K fixed by glauconite. Chaminade (5) observed that the same thing was true of  $\text{NH}_4$  fixed in a muck soil. According to Kelley and Jenny (23), grinding of micaceous minerals results in an exposure of the K ions originally held between the mica sheets. From the standpoint of the findings of Kelley and Jenny, the results of the French workers indicate that K is fixed between the layers of layer-lattice minerals.

#### SUMMARY AND CONCLUSIONS

The experimental evidence and discussions presented in the five papers of this series may be summarized as follows:

Fixed K is tightly held, resisting even the action of hot HCl of less than 0.1 *N* concentration. With acids of higher concentration, however, much (sometimes almost all) of the fixed K is liberated.

There is apparently no correlation between release of fixed K and solubilization of sesquioxides.

If fixed K is released without destroying the mineral which fixes it, it is possible to refix K in place of that released.

Although prolonged treatment of sericite with carbonic acid failed to free any K, continued electrodialysis did free some.

Common cations other than K and  $\text{NH}_4$  are not fixed.

The increase in fixation which generally follows liming is due not to the Ca but to the increase in the alkalinity of the soil system and the consequent effect on the relative base saturation of the exchange complex.

$\text{NH}_4$  is fixed in the same manner as K, and by the same mechanism.

In podzolic soils, fixation of  $\text{NH}_4$  and K takes place simultaneously.

The anion with which K is associated has, in general, no effect on fixation, except when carried out against a system containing appreciable exchangeable hydrogen. In the latter case there is an increase in fixation if a K salt of a weak acid is used; this increase is due to the tendency of the anion of the weak acid to combine with the hydrogen of the exchange complex.

When some of the exchange positions are blocked, fixation is reduced.

When K is forced to compete with other cations for exchange positions, fixation is reduced, the extent of reduction depending on the magnitude of the competition.

There is a linear relationship between the K which enters the exchange complex and that fixed.

No matter how great the application of K, the portion fixed is always less than the exchange capacity.

The fixing mechanism is the same for different materials.

Evidence is presented in support of the contention that K is fixed between the layers of layer-lattice minerals.

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## BOOKS

*Chemicals, Humus, and the Soil.* By DONALD P. HOPKINS. Faber and Faber, Limited, London, 1946. Pp. 278, plates 4. Price 12/6.

The purpose of the author of this book is to defend the use of fertilizers against attacks of the "humus school," represented by Sir Albert Howard, Lady Eve Balfour, F. H. Billington, and F. C. King. It is a carefully thought out presentation of the fertility problem and the part which both fertilizers and organic matter play in this connection. The need for the writing of the book is stated as follows:

Those who have fiercely attacked fertilizers in recent years have taken their case to the layman and it is not enough for orthodox scientists to retort that these matters have been settled for years. Perhaps it is true that they have been settled for a long time—but the ordinary man is not so sure because, unlike the scientists, he does not know which journals contain the authoritative accounts of research work, nor would he find these accounts simple reading if he tackled them. Responsible people tell him that fertilizers poison the soil, increase disease, and reduce nutritional values, and a case that he can understand within his own terms is set out. It is necessary for ordinary science to be similarly presented.

In contrast to those of the humus school, the author is eminently fair in his presentation, but he hews to the line and concludes that there is "no clash between chemical fertilizers and organic manures."

*Colonial Agricultural Production.* By ALAN PIM. Oxford University Press, New York, 1946. Pp. 190. Price \$3.

The purpose of this book is to consider colonial welfare with particular reference to agriculture. The colonies discussed are all in the tropics. Comparisons are made between the plantation and the peasant system. The subject is one of particular importance at the moment because of the notable advance in public opinion with regard to the responsibilities of the colonizing powers and the continued pressure of the peasant groups for a greater degree of independence. The essential point of difference between the plantation and the peasant system is that the plantation proprietor is concerned primarily with commercial production whereas the peasant thinks first of his own food needs and secondarily of crops that are offered for sale. It is apparent from the discussion that both systems will have to be continued, at least until such time as some type of cooperative approach to the solution of some of the problems of peasant farming can be developed by the educational process.

*Crop Production and Environment.* By R. O. WHYTE. Faber and Faber, Limited, London, 1946. Pp. 372, plates 32, figs. 53. Price 25s.

This book presents a survey of the subject of temperature and light in relation to vegetative growth and reproductive development of crop plants. Much of the discussion deals with one or another phase of vernalization and the theories



and facts related thereto. The allied subjects covered include growth, development, temperature, light, darkness, phasic development, environmental factors, hormones, plant breeding, crop distribution, and developmental physiology of crop plants. The bibliography contains nearly 700 references. This is a highly important and carefully prepared presentation that merits a place on the shelf of every worker in the field of plant science.

*Elements of Soil Conservation.* By HUGH HAMMOND BENNETT. McGraw-Hill Book Company, Inc., 1947. Pp. 406, figs. 114, graphs 14. Price \$3.

This book is designed to fill the need for a good text on soil and water conservation. The material is presented in an interesting and attractive form. It is easy to read. The illustrations are excellent. Where photographs would fail, graphs take their place. The nature and the seriousness of the problem are first presented and the remedies are then applied. The book is destined for a very wide reading by the public at large and will be found very useful as a text in the beginning course in soil conservation at agricultural colleges. It will probably largely replace the 968-page earlier work on "Soil Conservation" by the same author.

*Hidden Hunger.* By ICIE G. MACY AND HAROLD H. WILLIAMS. The Jaques Cattell Press, Lancaster, Pennsylvania, 1945. Pp. 286, figs. 17. Price \$3.

This is an interesting and instructive book dealing with the science of nutrition, choice and use of nutriments, poor nutrition, nourishment from the soil, the substance of life, food as eaten, food in action, food for work, food for fighting, and food for thought. The book covers a wide range of food problems from those of children to those of the folks who are in their "second forty years," and includes discussions of the feeding of armies and of the people on the industrial fronts. The chapter on soil considers such problems as soil decadence in relation to social and political decadence, soil conservation, abundance and deficiency of mineral elements, trace elements, and elements with toxic properties. Considerable space is given to food reinforcement. The book is designed for general reading but contains food for thought on the part of all scientists who are concerned with one or another of the many problems involved in human nutrition.

*Molds, Yeasts, and Actinomyceles.* Second edition. By CHARLES E. SKINNER, CHESTER W. EMMONS, AND HENRY M. TSUCHIYA. John Wiley & Sons, Inc., New York, 1947. Pp. 409, figs. 136. Price \$5.

This is a completely revised edition of Henrici's book of the same title that was published in 1930. Part of the revising was done by or with the help of the original author, particularly the first three chapters. Six of the chapters deal with the morphology, physiology, and taxonomic characters of the several groups. The others have to do with their biological activities with particular reference to fermentations and the diseases for which they are responsible. Of special interest are the 15 pages of tables showing the miscellaneous acids, metabolic products, and pigments produced by fungi. The last chapter gives a short review of antibiotics. A selected list of references is appended to each chapter. The book is an important contribution to the literature of the subject.

*Plant Growth.* By L. EDWIN YOCUM. The Jaques Cattell Press, Lancaster, Pennsylvania, 1945. Pp. 203, figs. 24, plates 16. Price \$3.

This book is designed for those folks who like to grow plants and want to know more about their nature and requirements. It begins with the seed and then proceeds with a discussion of its germination, the structure of the cells, the nature of protoplasm, the characteristics of roots, the absorption of water and mineral salts, the soil, the above-ground portions of the plant and their structures and functions, the control of insects, diseases, and weeds, hybridizing and other means of obtaining plant variation, plant hormones, the use of lime and fertilizers, light relationships, and rest periods. The amateur gardener will find the book of considerable interest and value in understanding what goes on in his soil and plants.

*The Production of Tobacco.* By WIGHTMAN W. GARNER. The Blakiston Company, Philadelphia, 1946. Pp. 516, figs. 81. Price \$4.50.

This book is the culmination of a lifetime of work primarily devoted to the tobacco crop. It deals with every phase of the production and use of this plant, including its botany, history, growing, curing, marketing, physiology, chemistry, and genetics. The material contained in the book should be of considerable interest both to producers and to consumers. Trends in consumption are of special interest, the total consumption being still on the increase, with cigarettes growing in popularity, snuff holding its own, cigars and smoking tobacco tending to drop, and chewing tobacco rapidly losing out. These trends may be of significance to the sociologist. The chemist and plant breeder will be intrigued by the many interesting facts about this highly popular plant that have been developed over the years by the specialists in this field. The book merits a place in every library.

*Rothamsted Experimental Station Report for 1939-1945.* Rothamsted Experiment Station, Harpenden, England, 1946. Pp. 270. Price 5/.

This report covers the war years. It gives a list of the trustees, council, and staff of Rothamsted, Woburn, Imperial College of Science and Technology, Agricultural Research Council Unit of Soil Metabolism, and The Imperial Bureau of Soil Science. The director's report includes a general review of the work done on soils and crop nutrition, soil moisture and cultivation studies, nodule bacteria, virus and fungus diseases, earthworms, insect pests, bees, statistical methods, and the classical field experiments and a list of publications, followed by more detailed departmental and sectional reports. It notes the retirement of Sir John Russell on September 30, 1943, and the appointment of Dr. W. G. Ogg, of the Macaulay Institute of Soil Research, to the directorship. The report contains a wealth of material of interest to every specialist in soils and crops.

THE EDITORS.



# SOILS OF INDIA: FOUR SOIL SURVEYS IN GWALIOR STATE

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The writer's interest in the soils of India stems from his experience in that area during the years 1918-1923, first as assistant director and subsequently as director of agriculture, Gwalior State,<sup>2</sup> Central India. Although it was evident that the soils of Central India varied widely and exhibited a number of unusual profile characteristics, the writer was so fully occupied with agricultural extension and administrative responsibilities that there was neither time nor opportunity for a serious, intensive study of the soils of that region. It was possible, however, to make general observations upon the broader groups of soils, particularly those of Gwalior State. In connection with official duties there were opportunities to do some little mapping of the soils of widely separated localities, in which a wide range of distinct series and types of soils were observed.

The Survey of India had long previously published topographic maps on the inch-to-the-mile scale of even the more remote parts of Central India.<sup>3</sup> More than a hundred quadrangles were needed to cover the region over which Gwalior State was scattered. When traveling in the state, the writer always carried these topographic sheets, mounted on cloth-backed plane-table paper. An assortment of colored pencils was also at hand for use in delineating soils information on the maps from time to time as additional observations were made.

During less frequent trips to Bombay, Madras, and Bengal Presidencies, and other regions outside Central India, the writer recorded large numbers of observations on general soil profile characteristics and land use methods in many other parts of India: slow trains with long and frequent stops afforded opportunities to examine the soil at wayside stations, and from the train window other soil and land use characteristics were observed and recorded.

## SOIL SCIENCE IN INDIA

As is indicated by the extensive bibliography presented by Wadia *et al.* (13), the literature on the soils of India is voluminous. The results of the numerous

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<sup>2</sup> Gwalior State is one of the Native States of Central India. The population was a little over 3 million in 1920. The area of approximately 25,000 square miles is about half the size of Iowa. Besides the Department of Agriculture, this state has its own Departments of Irrigation, Forestry, Revenue, Customs, Police, etc. Bordering and between different portions of Gwalior State are ten or more other Native States (small inclusions of Indore and Jaora States will be noted in the northwestern corner of map of the Mandasaur area).

<sup>3</sup> It will be noted on the soil maps accompanying this paper that the topographic maps used as the bases for these surveys were published in 1870, 1874, 1876, 1879, 1882, 1885, and 1891. With very few exceptions, these topographic maps proved to be remarkably accurate when used in the field.

and relatively intensive and significant physical, chemical, and microbiological studies upon Indian soils, especially in the laboratory and on the experimental stations, have failed, however, to give the reader interested in pedology and the development of soils a satisfying account of the principal kinds of Indian soils, their areal distribution, and relationships. Schokalsky's disappointing attempt (11) shows clearly that the observations and laboratory data which were available to her in Moscow in 1932 were quite inadequate to give a clear and useful idea of Indian soils to one who had not known them first hand in the field. Doubtless because of the wide range in quality of the observations and records at her disposal, her study was much less satisfactory than it might have been. Her experience shows that in India, as in other tropical regions, the enormous diversity in background and training of those recording the data on the soils in the field, as well as a lack of uniform use of many terms in pedology, has so confused the record that it is virtually hopeless to obtain a useful and connected account of the principal kinds of Indian soils from the information on record.

The writer doubts that it is worthwhile to attempt to assemble from the existing literature a useful, generalized soils map of India. On the other hand, a single trained soil surveyor, experienced in applying American soil survey practices in the field, with adequate funds for traveling expenses for a year's research through all the important parts of the country, could prepare a very useful generalized soils map of India as a whole. Such a soil map and its accompanying report would facilitate an understanding of the more strikingly different soils and land use practices of India and their relation to the climate. Even including the expense of drafting and lithographing a colored soil map and printing the report, the total cost would be a very small fraction of the amounts thus far spent on soil research in India.

A generalized soil map of India would be valuable not only as an aid in integrating and clarifying the results of past soil research, but also for those who are interested in the study of the soils of the world as a whole and who have no opportunity to study the soils of India in the field. It cannot be too strongly emphasized, however, that it would be unfortunate to first make a broad generalized soil map of India in an attempt to further a sound soil survey program. This is because in any generalized, necessarily small scale map the "great soil groups" along with "black cotton soils," "deltaic alluvium," "Indo-Gangetic alluvium," "laterite," "lateritic soils," etc. would almost certainly be the major units used. Such soil groups are invariably too broad and too inexactlly defined and understood to be useful for application agronomically. Moreover, if a scientifically sound and satisfactory soil survey is to result, the peculiar difficulties in classifying soils make it imperative to work from the particular to the general. It is believed that returns from soil research in India will be great following a reorientation of the approach, in which emphasis is placed upon soil classification in the field, employing the uniquely practical and relatively rapid United States Soil Survey methods. After the soils of a number of well-selected, representative areas of India have been mapped, a satisfactory general soil map can be made.

Huidekoper (2) describes the very detailed empirical field method employed in India for classifying and assessing "rent" (taxes) on agricultural land according to its value and capacity for producing the usual crops of the region. Local vernacular names were used for the various classes of soils. Since no correlation of the local groups between different regions was attempted, and since most of this "settlement" work in India was completed before the modern concepts of pedology had developed, the material collected can contribute but little toward a scientific understanding of the properties of Indian soils.

The writer had long hoped to present as nearly as possible a complete bibliography of the published work on the soils of India. But the ever-increasing number of papers on the soils of that subcontinent and the limited library and other facilities available to the writer, who had been working under pioneer conditions, made it continually more evident that in spite of the large amount of bibliographic material already collected, any such ambition would have to be abandoned. Subsequently, with the appearance of the extensive bibliography in India (13) and with the collected references published from time to time by the Imperial Bureau of Soil Science (3), the need for another bibliography became less urgent. Furthermore, none of the writer's material or records were available during the war. An annotated bibliography on soils and land use in India would, however, be of great value.

#### CENTRAL INDIA

Between 25 and 50 miles inland from the shore of the Indian Ocean, in the Konkan (coastal) region of Bombay Presidency, stand the high and rugged Western Ghats—a fault scarp marking the western limits of the Deccan Plateau. This plateau is built up of numerous horizontal layers of trap (basalt) flows; these originally covered more than 200,000 square miles, an area comparable to that of the Columbia River flows.<sup>4</sup> To the north and northeast, these flows extended into Central India far beyond Ujjain, into the Mandsaur area, and nearly to the Shivpuri area (fig. 1). Though, as a whole, the drainage of the trap region has been northeastward, eastward, and southeastward away from the Western Ghats, two strong rivers, the Narbada and the Tapti, flow westward into the Arabian Sea. That portion of the plateau north of the escarpment on the northern side of the Narbada Valley is the Malwa Plateau. This escarpment, with its highest elevations about 2,500 feet, is known as the Vindhya Mountains.

The drainage of the Malwa Plateau, as of the Mandsaur, Shivpuri, and Gwalior regions is northward and northeastward through the Betwa, the Sindh, and the Chambal Rivers to the Jamna River, thence to the Ganges.

#### *Climate*

The present climate of this semiarid part of Central India is characterized by a rainy monsoon season from June to September with about 30 inches of rain, ending with occasional showers in October. A winter season produces an oc-

<sup>4</sup> These flows poured out subsequent to the Middle Cretaceous (6).

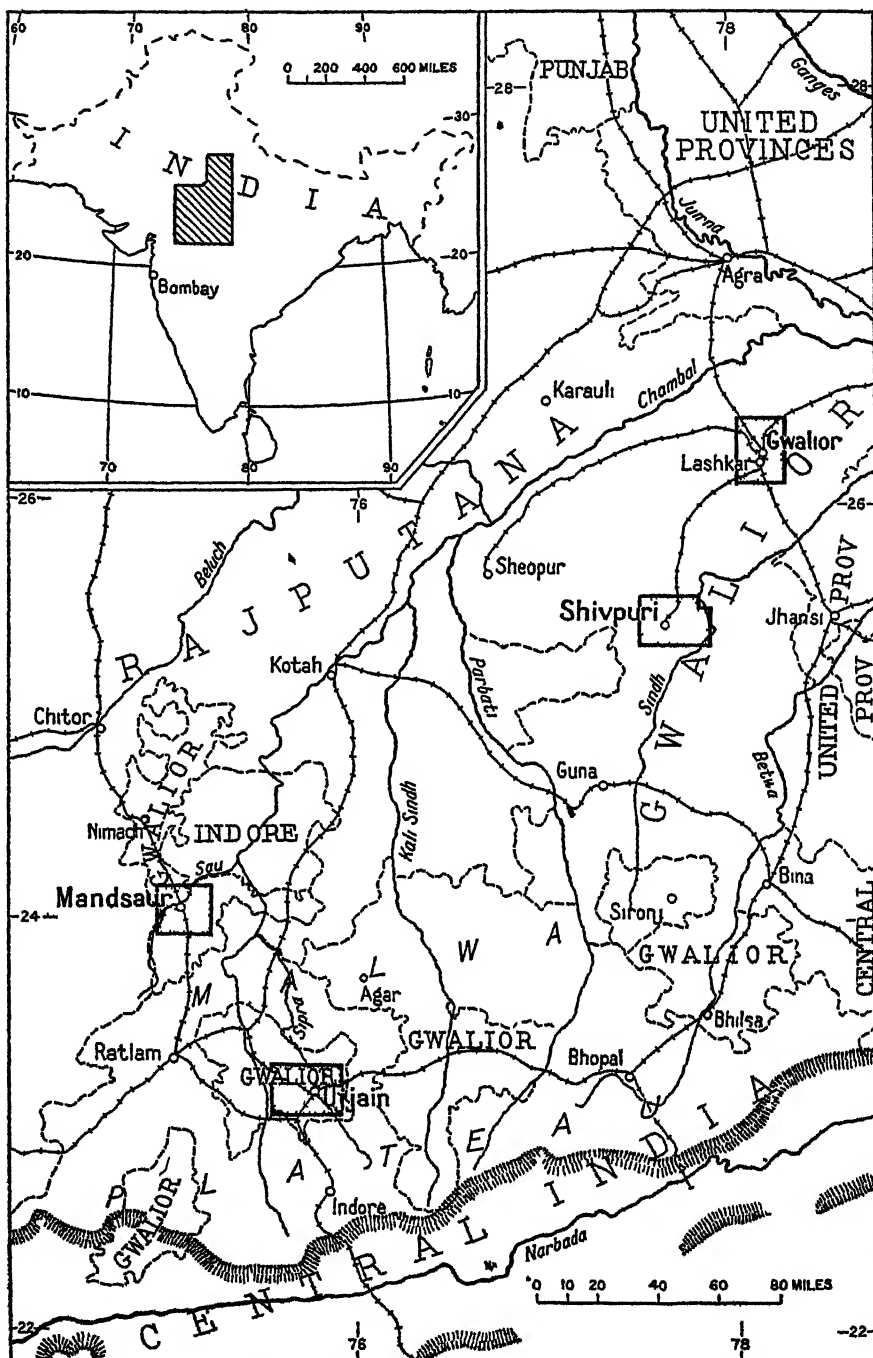


FIG. 1. LOCATION OF CENTRAL INDIA AND OF THE UJJAIN, MANDSAURY, SHIVPURI, AND GWALIOR AREAS

casional frost in December or January, and some years showers. There is a very hot, very dry season from March to May or early June. During this season local sandstorms, with very strong winds and showers, sometimes occur. The hot season is the cloudless one before the monsoon. In Malwa the rainy season, with its often heavily overcast skies, is relatively much cooler than Gwalior.<sup>5</sup>

### Vegetation

Low scrub forest and grassland appear to have been the natural climax vegetation over most of this semiarid region. The thorny *Babul* (*Acacia arabica*) is common along land boundaries; its hard wood is important for cart and farm tool making. When leafless and loaded with red flowers, the *Butea frondosa* trees are magnificent; these trees are useful because the flat shiny leaves are fastened together to make dinner plates. There is a better growth of trees along the deeper stream courses, especially in the Shivpuri area. Down over the Vindhyan escarpment, much of the rough terrain is well forested, with here and there clearings of the Bhils.

Although the mangoes and some other trees shed their old leaves and come out with fresh, tender leaves in the midst of the hot, dusty dry season, the most striking feature of the vegetation in Central India is the sudden change at the beginning of the rains. Then in a few weeks the whole country becomes green, and weeds and grass, as well as crops, grow with phenomenal rapidity.

### Soils

Gwalior State lies scattered over Central India, from close to the Nerbada River, across the Malwa Plateau with its soils from basalt and the Mandasaur region with its fossil laterite from a previous climate, across the Shivpuri Mountains with their diversity of soils on Vindhyan rocks, on northeast over the soils on the Gwalior formations, and out to the edge of the Indo-Gangetic alluvium. Here was a most unusual opportunity for the writer to study in the field a wide range of soils. A considerable diversity of soil conditions was found about each of four important centers, and there were also certain similarities between some of the soil series represented in the different areas.

#### SOIL SURVEYS OF FOUR SMALL AREAS IN GWALIOR STATE

The soil maps of the Gwalior, the Shivpuri, the Ujjain, and the Mandasaur areas were completed in connection with more intensive field trips in the country surrounding these important cities and towns. In the more remote localities, the field work was done on horseback, with mobile tent camps moved on bullock carts. In connection with the field work in these four areas, a comprehensive

<sup>5</sup> Since it is becoming increasingly evident that relatively small differences in the temperature and rainfall regime are of importance in determining the soil profile characteristics of tropical soils (5), it is indeed unfortunate that the meteorological data for these localities in Gwalior State are at present unavailable.



series of soil profile samples was collected of each of the horizons distinguishable in the field. The four soils survey maps accompany this paper.<sup>6</sup>

A series of studies (chemical, physical, and biological) had been planned for the comparison of the soil samples. For various reasons it was impossible to complete this program of laboratory studies; nevertheless, certain results have been obtained which will be included in subsequent papers in this series.

#### DESCRIPTION OF THE AREAS

In considering the several areas, we shall begin with the southernmost, the Ujjain area in the Malwa Plateau, where the soils and their parent rocks are the simplest. Next, we shall proceed to the Mandsaur area, where the principal soils and rocks are similar to those of the Ujjain area, but where there are also soils from sedimentary rocks and conspicuous occurrences of laterite. Third, we shall go on to the Shivpuri area, with its diversity of soils from sedimentary and intrusive rocks. Lastly, we shall consider the Gwalior area with some still different parent materials, and where the principal soils are on tongues of the vast North India plains.

#### *Ujjain area*

As is often the case in the Deccan, the basalt in the Ujjain area has eroded in places in a somewhat steplike manner, leaving flat-topped mesas with vast expanses of gently undulating plains in between: "a land of wide rolling downs dotted with flat-topped hills" (2). Elevations in this area vary from 1,727 to 1,804 feet on the mesa tops, while on the rounded divides the range is from 1,623 to 1,667 feet above sea level.<sup>7</sup> Ujjain town, perhaps 40 feet above the Sipra River bed, is reported to be 1,679 feet above sea level. After the main stream valley developed in the basalt, secondary alluvial deposits filled in the lower parts of the valleys to a depth of 30 or more feet; catastrophic erosion subsequently removed much of these deposits, forming severely gullied "bad lands."

<sup>6</sup> Shortly after completing these four surveys, the writer left India for service in the Philippines, where the maps were subsequently lithographed. The drafting was done by Filipino draftsmen of the Topographic Branch, Coast and Geodetic Survey, Manila; the lithographing was done under the supervision of S. H. Wilson, by Carmelo and Bauermann, Manila. These soil maps were only recently verified as being in the Soil Science stockroom, New Brunswick, N. J.

Not long after the lithographing was completed, the writer left for China for a 2 years' detail; he then returned to the Philippines, and finally went to Siam. For 5 years following Pearl Harbor the field notes, data, and certain references necessary for preparing this and subsequent papers were unavailable. Thanks to loyal Siamese associates, during the summer of 1946 the notes and data were recovered in Bangkok and packed for shipping to the United States. Because of amazing errors in ocean freight shipping, these data failed to arrive until this paper was in press; they will be used in preparing subsequent installments.

<sup>7</sup> There is little ground water to be obtained in the basalts of the Ujjain region. From a boring some hundreds of feet deep near Ujjain, no material change in the rock was reported. In the villages it is customary to dig rectangular wells, sometimes as large as 20 by 40 feet, 20 to 30 feet into the rock. Water slowly seeps out of cracks in the rock and accumulates in the excavations.





Malwa clay loam and clay loam adobe<sup>8</sup> (often known as "regur" or "black cotton soil" group) had developed on all but the steepest portions of the basalt. This soil is a dark grayish brown, or dark brownish gray to almost black, from less than 1 foot to more than 6 feet deep. In some cases the basalt breaks down directly into small fragments, 1 to 3 cm. in diameter, called "murrum"<sup>9</sup>, and these weather to black clay loam. In the eastern and northeastern parts of Ujjain area, where the rock apparently is harder, the unit fragments of the rock seem to be roughly ten times larger. Weathering by exfoliation, these fragments become rounded, and though occurring on the higher part of the terrain are popularly believed to be stream-rounded cobbles. Since only a single rock type and secondary accumulations from that rock are the parent materials of the soils in the Ujjain area, the soil pattern is very simple. Fragments of chert and agate, from 1 to 3 inches in diameter, and some geodes, are rather common in this soil. Though Malwa clay loam and clay loam adobe have weathered directly from the rock, Sipra clay loam has developed on the eroded secondary deposits in which petrologic and pedologic patterns are more complicated. It is light grayish brown, medium brown, or dark brown and somewhat eroded instead of uniformly sloping or level, thus differing in two respects from Malwa clay loam. Sipra clay loam produces good crops of sorghum in the rains, or wheat in the winter.

When not too wet, the heavy Malwa clay loam soil is friable and self-mulching. Plows are seldom used—the most common cultivating tool is a "blade-harrow" (*bakhar*) like a weed cutter. This is an iron blade about 18 inches long so fitted to a wooden frame and pole that the blade has a downward tilt to hold it in the soil. This tool is drawn by a pair of bullocks. Deep soil rotation is effected through much of the fine surface mulch falling into the wide and deep cracks during the dry season. The Indore Cotton Experiment Station, where Howard developed his process of composting (1), is not far from Indore town, and about 30 miles south of Ujjain. As he says, these Malwa clay loam soils "plough and subsoil themselves."

Quite distinct from the grayer soils farther away from the river is the yellowish brown, light brown, or light yellowish brown Ujjain loam, which occurs as terraces in the gullied zone, about  $\frac{3}{4}$  mile wide, mostly along the Sipra River. This loam is as much as 10 to 15 feet deep with no marked accumulation of calcium carbonate or other profile development. Areas of this soil have been seriously eroded by the side streams.

#### *Mandsaur area*

Mandsaur town and area are 80 miles west of north of Ujjain, just on the northwestern edge of the Deccan trap flow. As is evident from the soil map,

<sup>8</sup> Following an early practice in the U. S. Soil Survey, the term "adobe" was used to indicate that during the long dry season the surface soil breaks down into a finely granular mass. Simultaneously with the development of this mulch, wide cracks develop which are often several feet deep.

<sup>9</sup> Unfortunately, G. Milne in writing on the soils of East Africa (4) used "murrum" for "concretionary ironstone."

beyond the igneous rocks are exposed geologically much older sandstones and shales.<sup>10</sup> As would be expected, the elevations above sea level in the downstream Mandsaur area are lower than those in the Ujjain area. The hills vary from 1,656 feet in the southeast to 1,482 feet in the northeastern parts of the area, with intermediate elevations between 1,416 and 1,460 feet. Mandsaur town, at 1,514 feet, is on an outlier of sedimentary rock, while the mesa on the sandstone in the northwestern corner of the area is 1,770 feet above the sea.

In addition to the Malwa, Sipra, and Ujjain series developed from the basalt and its derivatives, Mandsaur loam and stony loam also occur<sup>11</sup> (being climax soils of the present rainfall regime, these soils are pedocals). These more slaty shales give rise, at least under Mandsaur conditions, to different sorts of soils from those developed from the shales in the Shivpuri and Gwalior areas. The very shallow sandy soils on the sandstones of the Delhi and Aravalli formations in the northeastern and northwestern corners of this area are of the same series as the soils from Vindhyan sandstones in the Shivpuri and Gwalior areas.

The most interesting soil group in the Mandsaur area is the laterite. As it now occurs here, it is the illuvial horizon (often called the "B horizon") of a laterite soil, the upper layers of the profile having been lost by erosion. It is to be noted that "laterite" is here used in the sense of Buchanan's description and as the word has been used ever since by those who have to do with it in India and neighboring countries (8,10). Although Oldham's differentiation of high level and low level laterites cannot be maintained, his description of the material is excellent. As Oldham points out (6, p. 256), the laterite capping the basaltic mesas was formed shortly after the cessation of the lava flows, generally believed to be in the Tertiary. He continues (6, p. 376): "It is difficult, in presence of the great amount of denudation which has taken place since the laterite caps were part of a more extensive formation to escape the conviction that the high level laterite must be of considerable geological antiquity." This laterite developed when the prevailing climate was humid tropical: presumably before the Western Ghats cut off much of the monsoon rains, making the climate here semiarid. In other directions, sedimentary formations indicate that seas were much closer to what is now the Malwa Plateau than at present. It seems clear that some similar juxtaposition of laterite from a former humid tropical climate in parts of Africa which now have a climate under which chernozems are the climax soils was what confused Marbut (12, pp. 201 ff.) in his ill-advised endeavor to interpret the soils and climates of that continent from the literature. As Oldham emphasizes (6, p. 383, 386), laterite always develops on a continuous, level, or almost level, surface. All of the intervening basalt on these levels has been weathered, therefore, and carried away by erosion, leaving only certain mesas of basalt still capped with laterite.

Occasionally we came across slag heaps where the laterite had been smelted to obtain the iron. Undoubtedly this smelting was done when fuel was more

<sup>10</sup> Geologically, these formations belong to the Delhi and/or Aravalli series (8). But for the pedologist, petrographic character is the important matter, not geologic age.

<sup>11</sup> On the soil map some of the soil bodies of this series are incorrectly colored.





plentiful than it is now and before imported iron could be purchased relatively cheaply.

### *Shivpuri area*

About 190 miles northeast of Mandsaur and north-northeast of Ujjain is Shivpuri, the summer capital of Gwalior State. Formerly known as Sipri, before the age of railways it was an important town on the Agra-Bombay military road. The elevation of the undulating uplands surrounding the town is about 1,700 feet, which is sufficient to give some relief from the very hot weather at Gwalior and elsewhere on the plains.

The Deccan trap does not come within many miles of the southern edge of the Shivpuri area. In this area the rocks are thick alternating strata of quartzitic sandstone and shales belonging to the Vindhyan or upper older Paleozoic formations (6), which dip very slightly to the west. The form lines of the base map show rather well the general character of the topography.

To the west of Shivpuri town is the highest formation, a shale, upon which has developed Singanwas clay loam. The dark brownish gray soil is 1 or more feet deep and in places has some small scattered iron concretions; the subsoil is yellowish brown *kankary* (gravelly) loam. The areas of this soil are extensively cultivated.

Darauni loam has developed on the accumulated soil materials in the depressions; the soil has catastrophically eroded in various places. It will be noted that in the Shivpuri area it is only around the edges of this body of shales and its associated soils that bodies of laterite occur. Just east of the railway terminus at Shivpuri the surface soil of this laterite is dark red gravelly loam, 4 to 5 inches deep. Below this is red loamy gravel of rounded and angular gravels and concretions. It is probable that this laterite developed in Tertiary time, when the climate was humid tropical, during the same time that the laterite developed in the Mandsaur area, and in many other parts of Central India, such as Agar, Guna, and Saugor. The topography of the region was most likely that of a peneplain.<sup>12</sup> The associated Shivpuri and Nohri loams and clay loams are perhaps in part degradation and alteration products from former larger bodies of laterite.

The hard quartzitic Vindhyan sandstone which lies below the shales is exposed to the east of the Shivpuri soils. The light fine sandy loam soils on these rocks are rather shallow.<sup>13</sup> This land, occupied by low forest and thick brush, is not worth cultivating. Some pasture is obtained, and in places the grass may be gathered for emergency fodder during famines and hauled 75 or more miles by bullock cart.

<sup>12</sup> British cantonments, in the days of military occupation of this region, nearly a century ago, were almost invariably located on mesas of laterite. These were not only topographically preferable, being well drained, but in contrast to the soils developed under the now prevailing climate, are not muddy even during rains.

<sup>13</sup> The source of the iron in the numerous round iron concretions in this soil is very puzzling. Very likely the materials from which the iron was derived were wind-borne.



The eastern edge of this quartzitic sandstone is an irregular escarpment, on the lower slopes and at the foot of which are the Mohona loam and shaley loam on shales derived from formations that underlie the sandstone. Where the topography is nearly flat, soil development has progressed further; here the soil is Singanwas clay loam. These are planted to sorghum and millet in the rains; where irrigation water is available, wheat is raised during the winter season. As in other valleys farther west, where material from the Singanwas soil group has gradually worked out into the Surwaya Valley, Baghora clay loam has developed.

East of this roughly north and south zone of soils from shales, appears another north and south zone of Vindhyan quartzitic sandstone, which farther west is beneath the shales. On much of this sandstone the light fine sandy loam soil is so shallow that the low scrub forest is used only for pasture. In some places on these sandstones and in many places along their eastern escarpment, however, the soil is deep enough to be planted to a rains crop. These places have been shown separately on the map as Surwaya fine sandy loam. This type, however, is not of much use for crop production. East of the Sindh River is a slightly different and slightly better soil type, Bundelkhand sandy loam, on which are two villages, suggesting a somewhat less poor soil. It is believed to be related to the Bundelkhand gneiss<sup>14</sup>—the predominant rock over a large region east of the Sindh River.

#### *Gwalior area*

About 75 miles by road north-northeast of Shivpuri and 320 miles north-northeast of Ujjain by road is Lashkar city, the capital of Gwalior State. Lashkar stands at the southern foot of a long and narrow sandstone mesa, "The Gwalior Fort"<sup>15</sup> about 300 feet high, which dominates the town and plain. The sandstone of this mesa is quartzitic Vindhyan; to the west are many hills of this same rock, with its infertile, shallow, fine sandy loam soils. As suggested by the form of the hill in the northeastern part of the Gwalior area, this sandstone is not quite so nearly flat in this locality.<sup>16</sup> In the center and southern parts of the area appearing below the sandstones are the "thin, flaggy, siliceous, ferruginous shales, copiously interbanded with hornstone and jasper, frequently of a brilliant red color" (6, p. 65) characteristic of the Gwalior formation,<sup>17</sup> which form the hills mapped as Gwalior rough stony land. Gwalior silt loam, which had developed in the valleys between the areas of Gwalior rough stony land and around the bases of the hills in the central part of the area, is likely loessal in origin, reworked somewhat by stream action. In recent times a lowered base level of the streams and intensified use in pasturing cattle and especially goats

<sup>14</sup> As Oldham states (6, p. 26), this rock is to all appearances a perfect granite.

<sup>15</sup> This mesa, roughly  $1\frac{1}{2}$  by  $\frac{1}{2}$  miles, was strongly fortified in the 15th century and has some lovely buildings of that period. At the northern end of the fort is the older city of Gwalior.

<sup>16</sup> This is a remarkable sandstone. Beams of it, more than 40 feet long, quarried not far northwest of Gwalior, are used as horizontal supports for flat masonry roofs.

<sup>17</sup> The Gwalior formation is placed in the Transition Systems which are earlier than the Older Paleozoic (6, p. 47), thus just younger than the Bundelkhand gneiss to the south.





have resulted in very serious gulying. In the northern and northeastern parts of the Gwalior area are the plains of the older alluvium which are continuous with the plains of the Ganges Valley.

In the Gwalior area several series of soils have been differentiated. Morar clay loam is a climax pedocal developed under relatively well drained conditions from a parent material low in quartz sand. Susera silt loam and very fine sandy loam, as the name suggests, contain a considerable proportion of very fine quartz sand and silt, and are less well drained. Portions of this soil group are saline. Muscovado sugar made in open kettles from sugar cane grown with irrigation on some of these previously idle saline portions was so salty as to be useless for food. Roughly crescentic earth dams ("tanks") hold the rain water on the land so that winter (*rabi*) crops can be grown. Nurabad fine sandy loam is brown, well-drained, and in places has been drifted by the wind into small dunes.

#### KANKAR IN SOILS OF CENTRAL INDIA

The *kankar* (concretionary calcium carbonate<sup>18</sup>) horizon in the subsoil of many of these soils, at about 1 m. depth, clearly indicates that Central India is now a region where pedocal soils develop. In the soils of the Gangetic alluvium, in a part of the Gwalior area, the individual calcium carbonate concretions vary in size from that of a hazel nut to that of one's thumb. Sometimes the concretions are very irregular, knobby, or branched. In other places the *kankar* horizon is almost a calcareous tufaceous hardpan. In Malwa clay loam the concretions are more nearly round and from the size of a hen's egg to that of a double fist. By contrast, the soil-forming conditions during at least part of Tertiary time developed pedalfers; witness the fossil B horizon of former laterite soils which still cap some of the basalt buttes in the Mandsaur area, and the bodies of laterite in the Shivpuri area.

In the plains of North India, *kankar* has been generally used for gravelling the roads, and what unusually dusty roads it makes! *Kankar* is the only source of building lime for tens of millions of Indians. It is mined from the illuvial horizon of many of these soils and pounded to remove most of the adhering soil; then a heap many feet high is made, with alternate 6-inch layers of *kankar* and dried cattle dung cakes; and the fuel is ignited. After smouldering for many days or weeks, the heap finally cools. The *kankar* is then ground in a crude stone roller mill—a stone trough in the form of a ring in which a narrow, heavy stone roller, on a heavy beam for an axle pivoted at one end, is pulled around by a pair of oxen. From time to time water is added to the trough in which the roller runs; this helps to slack the *kankar*. Sand is subsequently added; this mixture is the mortar for the very generally used stone masonry building construction.<sup>19</sup>

#### SOIL FERTILITY MAINTENANCE AND FERTILIZATION

In a rural society where the peculiarly compelling customs and taboos of the Hindu religion dictate virtually every phase of human life and activity to a

<sup>18</sup> *Kankar* originally meant gravel or small rock fragments (6, p. 436). <sup>9</sup>

<sup>19</sup> Quick lime for whitewash and for chewing with the betel leaf and areca nut is imported from other parts of India where limestone is found.

degree unimagined by an Occidental, and particularly where these are compounded with the trickery of a short-sighted landlord (9), soil fertility maintenance on a sound scientific basis is an especially difficult problem.

The most difficult phase of this problem for Central India is that practically all the rural folk are Hindus. They consider cattle sacred and are strongly opposed to permitting them to be killed for any reason.<sup>20</sup> Thus the cattle population is much higher than necessary and is reduced only by death during famines. Since there is seldom adequate fodder for the cattle even in the good years, not only is all the wheat and other straw and farm roughage fed to the cattle, but also quantities of *dub* (*Cynodon dactylon* Pers.) and other roadside grasses and weeds are laboriously scraped up with a *kurpi* (a square-ended trowel), carried home, and fed to the animals; when fodder is especially scarce, branches of shade trees with palatable leaves are lopped off for the animals to browse.

Most of the farmyard manure is carefully collected, even from the draft cattle at work in the city streets. The dung is made into cakes (*khandis*) sometimes with an admixture of leaves, straw, and other farmyard trash. These cakes are dried in the dooryard or slapped on the mud walls to dry. These *khandis* are the principal domestic fuel for the kitchen. Only in a few wealthy homes is charcoal used for cooking and other domestic heating.

Even the farmers live and keep their cattle, carts, plows, and other tools in villages of single-storied, mud-walled, tile-roofed houses. Behind the houses are small mud-walled yards where the farm gear and harvested crops are kept, and where the family can live and work without being seen by others. Some of the fresh cow dung is mixed with earth for smoothing and plastering the mud walls. Frequently, groups of houses are occupied by a certain caste, scavenger and other outcaste groups having their groups of houses around the periphery of the village. The lanes between groups of houses are wide enough for the ungainly ox carts to get through. Too often ashes and other waste and sweepings from the houses are not carried as far as a refuse heap on some vacant spot in the village—they are just thrown into the lane in front of the house. But since the villages are always on a slight knoll or artificial elevation, during the summer rains the wash flushes the lanes; in the dry season the wind helps. Throughout the year, the poultry, and particularly the hogs belonging to the outcastes, work the refuse over very thoroughly. Close about the villages the fields usually have some crops for cover, and there the villagers defecate, thus increasing the fertility of a narrow zone immediately about the villages (1).

Thus the mineral nutrients tend to accumulate in the lands in and close to the village. Where there is a well that can be used for irrigation, sugar cane or some other more intensive crops may be grown on these more productive soils; groups of mango trees are common. But seldom is manure or other wastes ever put back on most of the fields which are cropped annually.

The only consolation is that the farmyard manure is markedly lower in plant nutrients than the dung of temperate-zone animals which have been fed consider-

<sup>20</sup> No cattle could be butchered for beef in Gwalior State; we were not even permitted to kill a ham-strung bull that wandered around our experimental farm.

able proportions of concentrated feed. Indian cattle often get little else to eat than finely broken wheat straw and some chopped sorghum stalks.<sup>21</sup> Both the cattle and the human population exist on relatively very meager amounts of nitrogen.

During the writer's time in Central India commercial fertilizers were not used; on the contrary, phosphorus was being exported from that region. Occasionally, heaps of hundreds of tons of weather-beaten bones were noted at railway sidings awaiting grinding for shipment out of the country.

Thus it is a mystery how the soils of Central India continue to yield even the fair crops that they do, century after century. Doubtless the 10 to more than 15 plowings with the native plow at the end of the rains are important in this connection. It is no wonder that photo-fixation of nitrogen continues to be postulated as one of the reasons why those soils are not even less productive.

#### CROPS

Since Central India is a semiarid region, rice (*padi*) is not grown here. What little is consumed by the well-to-do is imported. The principal food of the wealthy is whole wheat flour kneaded with water, pressed thin, and heated on a piece of sheet iron; the vast majority of the Indians in Central India eat similarly prepared thicker masses of ground sorghum or *bajra* (giant millet).

At the commencement of the summer rains a mixture of tall grain sorghum (*jowar*) and giant millet (*bajra*) is broadcast in the fields. When the crop is about half grown, it is plowed with the light wooden plow instead of being thinned. If the rains are heavy, the millet does better; if the rains are light, the sorghum does better. In the Ujjain region on Malwa clay loam, the "black cotton soil," cotton is also planted. Particularly in Malwa, sorghum and pigeon pea (*Cajanus indicus*, *arhar*, *tour*) may be drilled together. The sorghum is harvested early, after which the pigeon peas commence to grow and are harvested in March. Sesamum is another rains (*kharif*) crop.

#### Winter (*rabi*) crops

Wheat is the most important winter crop. Earth dams on slopes or in shallow valleys form "tanks" (ponds) an acre or more in area. In October the water is released, moistening the fields below. Wheat is then planted in the bed of the pond and on the moistened land below. Gram (*Cicer arietinum*) is planted in October as a winter (*rabi*) crop.

#### Irrigated crops

The usual source of irrigation water for sugar cane and garden crops is wells, though larger dams for the storage of irrigation water have been built near

<sup>21</sup> When the writer was spending some time at the Imperial Agricultural Research Institute, Pusa, about 1921, F. J. Warth was just commencing nutritional studies on Indian cattle, weighing and analyzing all food and excreta. He reported in personal conversation how amazed he was that almost no nitrogen was voided—that he would not have believed the results if he had not with much care done all the work himself.

Gwalior, Shivpuri, and Ujjain. The Chambal, Sindh, and other large rivers are too deeply entrenched into the plain to serve as sources of irrigation water for the plains.

Mangoes are an important roadside tree; the fruit, however, is most disappointing—a bundle of coarse fibers saturated with a very turpentiney juice. Neem (*Melia* sp.) is another important roadside tree. The oilcake from pressed *Melia* seeds is a useful fertilizer, especially for sugar cane, for the bitter flavor seems to deter the termites from damaging freshly planted sugar cane cuttings. Betel vines (*Piper betle*) seldom do well unless protected from the hot, dry winds by means of high masonry walls and a "lath" roof. The betel leaves are chewed with areca nuts (*Areca catechu*), ground acacia bark, lime, and condiments.

At least for Central India, Schokalsky's crop map (11) is very inaccurate.

#### SOIL EROSION

As is evident from the accompanying soil surveys, gully erosion is serious in all four areas. Even worse and more extensive gullied badlands lie along the Chambal and Sindh Rivers northwest, north, and northeast of the Gwalior area. In 1920, Maharaja Scindia set up a commission for the study of the problem of soil erosion and the means which might be adopted for its control; the writer was one of the three members who spent more than 6 weeks on horseback, mapping the eroded area and studying local methods of control. We found that the loss of arable land by erosion was very serious; in many cases erosion was being aggravated by the overpasturing with goats. The masonry dams which in some cases had been built in the ravine bottoms were not only quite futile to retard the erosion of the uplands, but were usually so inadequately designed that in a few years the stream washed out around them. Smithies and other foresters of the United Province Forest Department had experimented extensively with methods of retardation of the erosion and possible reclamation and reforestation. They showed (7) that fencing to conserve the grass cover and prevent excessive tramping of the soil by animals was extremely important. Digging down of the steeper slopes, planting of *babul* (*Acacia arabica*) on the slopes and of *shisham* (*Dahlbergia sissoo*) in the moister bottoms, combined with suitable earth dams and protected spillways were the most effective methods of control of erosion and land utilization. Adequate police protection was most difficult because of the pressing need of the populace for fuel and timber for house and cart construction and for fodder for the excessive numbers of livestock.

#### SUMMARY AND CONCLUSIONS

As a basis for the interpretation of numerous soils data, a satisfactory generalized soil map of India has yet to be made. Only by starting with soil series and types or similar lower categories can a sound classification and map of the soils be made. As a contribution to such a general understanding of the soils of India, the four accompanying relatively detailed soil survey maps were made of small areas in Central India.

Some striking characteristics of the soils mapped and of the region as a whole

are given: the easy granulation and deep cracking of Malwa clay loam are agriculturally of importance; the relation of the laterite-capped mesas to the pedocal soils now climax in the region; the abundant calcium carbonate concretions which are mined, burned, and ground into mortar for use in masonry construction.

Soil fertility relationships are affected by religious considerations, resulting in far more cattle than are necessary or useful. The lack of other fuels than cattle dung and the feudal system of tax collection are added handicaps to maintaining soil fertility at a more satisfactory level.

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# OCCURRENCE OF SELENIUM IN SOILS AND PLANTS OF COLOMBIA, SOUTH AMERICA

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In 1936 the Agricultural Society of Colombia sent a soil sample<sup>2</sup> from a place called "El Peladero," Sutamarchán, State of Boyacá, for analysis to the Laboratorio Químico Nacional. In 1939, a farmer from the Leiva District, in the same state, sent another sample. Both indicated that cattle, poultry, and even

TABLE 1

*Description and selenium contents of soils and plants from the Leiva District, State of Boyacá, Colombia*

LABORATORY NUMBER	DESCRIPTION OF SAMPLES	SELENIUM CONTENT
		<i>p.p.m.</i>
	A. Gray-brown silty clay loam, from wheat field	
11.820	Depth of sample 0-12 inches	6.0
11.821	Depth of sample 12-35 inches	3.5
	B. Grayish brown clay loam, from barley field	
11.822	Depth of sample 0-12 inches	4.5
11.823	Depth of sample 12-30 inches	7.0
11.824	C. Subsoil (gray clay) from badly eroded area	2.5
11.825	D. Exposed gray shale	14.0
11.826	E. Shale taken in deep gully, salt-incrusted	1.0
11.827	F. Peas, near soil A.	135.9
11.828	G. Barley from field of soil B	137.3
11.830	H. Seed of <i>Tara Spinosa</i> (Mol.) B. and Rose, a legume	8.6

humans were suffering from chronic diseases and that the cattle and humans were loosing their hair. When routine chemical soil analysis failed to reveal characteristic deficiencies, minor elements were taken into consideration. Qualitative tests revealed the presence of significant amounts of selenium.

<sup>1</sup> The author acknowledges the assistance of L. A. Rojas-Cruz in the analytical work.

<sup>2</sup> Laboratory sample 560 (1936).

In 1945, soil and plant samples collected<sup>3</sup> in the Leiva area were analyzed<sup>4</sup> for selenium according to the methods used in the United States (1, pp. 10-12, 132; 3; 6).

Table 1 gives the descriptions of the soil and plant samples and the selenium contents.

Without exception, the selenium content is high, in some cases very high. These findings have been confirmed on samples from the same locality by Lakin,<sup>5</sup> and also by Robinson and Edgington (4), who wrote: "We have recently found as high as 110 p.p.m. Se in peas and 155 p.p.m. in wheat grown in Colombia, South America."

Normal soils, as a rule, contain 0.3 p.p.m. selenium or less.<sup>6</sup> Although a high total selenium content is not necessarily an index of toxicity, the fact that all plants, especially peas and barley, are high in selenium may be taken as an indication of a high degree of availability of soil selenium. Trelease (5) cites experiments with rats which indicate that food containing as little as 5 p.p.m. of selenium stunts the growth of the animals and that about 20 p.p.m. is lethal. In the light of these observations and Byers' (2) statement that a selenium content of more than 4 p.p.m. in a dry diet is definitely injurious, diseases in animals and humans are indeed to be expected in Sutamarchán and Leiva. Further investigations are under way.

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<sup>3</sup> By H. G. Lewis, of the U. S. Soil Conservation Service, and Alberto Franco, of the Caja de Crédito Agrario, Bogotá.

<sup>4</sup> With the aid of special glass apparatus supplied by the U. S. Department of Agriculture through the courtesy of H. G. Byers, whose cooperation is gratefully acknowledged.

<sup>5</sup> Private communication, December 11, 1945.

<sup>6</sup> EDITOR'S NOTE: This upper limit appears somewhat high for soils of the United States. It seems probable that selenium can be detected in any soil, but the quantity present seldom exceeds 0.1 p.p.m., and soils in semiarid regions with 0-2 p.p.m. selenium have produced very toxic plants.

# EFFECT OF MICROORGANISMS ON PERMEABILITY OF SOIL UNDER PROLONGED SUBMERGENCE

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Pumping for irrigation in the San Joaquin Valley, California, has been practiced for many decades over rather large areas. This practice has continuously lowered ground-water levels in many of these areas because the rate of replenishment has not kept pace with the rate of removal by pumping. Consequently, the pumping rate must be decreased in the affected areas or a way found for increasing the rate of recharge of the underground reservoir. Through the operation of the Central Valley Project, surplus water resulting from high stream flow will be available at certain times of many years. If stored underground, this will not only replenish the depleted ground-water supply but also conserve it for future pumping at a time when surface supplies are limited.

Water-spreading (5, 9) for underground storage has been practiced to a limited extent in southern California in natural river channels, on debris cones and fans, and on soils composed primarily of sands, gravels, and cobbles. In the San Joaquin Valley, however, spreading operations will have to be carried out on agricultural soils of the valley floor between the major stream channels. The soils in such areas where underground recharge is likely to become an important practice are permeable loamy sands and sandy loams belonging to many soil series.

Preliminary field studies of water-spreading<sup>3</sup> have been carried on in Kern County, California, for several years by the North Kern Water Storage District on Exeter and Hesperia sandy loams. Kern River water was applied to experimental ponds of about 0.01 acre (20 by 20 feet) as well as to fields up to 60 acres. This study indicated that although the initial infiltration rates were satisfactory, ranging in general from 3 to 4 feet depth of water daily, the rates decreased with time, rapidly at first and then more slowly. During the period of rapid decrease, the rates dropped about 50 per cent every 12 to 20 days, with an average of 16 days for all ponds concerned. With continued operation the infiltration rates declined slowly, often to but a few inches a day, and for all practical purposes the ponds "sealed up." Thus the spreading operation, although satisfactory at first, became uneconomic within a relatively short time. Field tests and observations on this problem are still in progress.

<sup>1</sup> Associate soil technologist. The author wishes to acknowledge the cooperation during the initial phases of this investigation of J. E. Christiansen, formerly irrigation and drainage engineer, and W. P. Martin, formerly associate microbiologist.

<sup>2</sup> Contribution from the U. S. Regional Salinity Laboratory, Riverside, California, Bureau of Plant Industry, Soils, and Agricultural Engineering, Agricultural Research Administration, U. S. Department of Agriculture, in cooperation with the eleven western states and the Territory of Hawaii.

<sup>3</sup> Haehl, H. L. Unpublished data on water-spreading. North Kern Water Storage

The laboratory investigation<sup>4</sup> reported herein was undertaken to determine the reason for the decreasing rate of infiltration under continuous submergence.

#### EARLY STUDIES ON PERMEABILITY

The initial studies at the Regional Salinity Laboratory on the over-all problem were conducted by Christiansen and Magistad,<sup>5</sup> who attempted to obtain answers to several important questions relating to problems of water-spreading on agricultural soils. Permeability tests under prolonged submergence were made on 43 undisturbed soil cores (4) and on numerous disturbed samples of soil taken at various locations in the upper San Joaquin Valley. Most of the soil cores were obtained in steel cylinders 5 inches by 36 inches, but a few were taken in 4½-inch by 16-inch lucite cylinders. Some of the results of this investigation have a direct bearing on the present study.

A study of the disturbed samples taken at various depths in the soil profile showed *the surface 12 inches or less to be the zone of limiting permeability*. This is the section of the soil that contains most of the organic matter, and considerable significance is attached to this fact. These results were verified on undisturbed soil cores 36 inches long having a system of manometers attached at various distances between top and bottom of the cores. When a certain core was inverted during the test it was found to be least permeable at the bottom, which in this case was the surface horizon of the field soil. In a few cases, however, the permeability of the soil cores as a whole was limited by hardpan or by horizons of high density at some distance below the surface.

When soils are continuously submerged and the daily permeability or infiltration rates are plotted against time, the S-shaped curves obtained, as exemplified in figure 1, indicate progressive change in permeability throughout the test. Generally there is an initial decrease followed by a marked increase to a maximum permeability, which in turn is followed by a considerable decrease. This trend holds for field as well as for laboratory tests, because the rate of water infiltration into the soil when completely saturated is a function of the least permeable horizon in the profile. These changes are explained (1, 2) as follows:

*Phase 1.* After initiating field or laboratory tests, the permeability decreases to a minimum. On highly permeable soils this initial decrease is small, or nonexistent, but for relatively impermeable soils, it may be appreciable and continue for 10 to 20 days before the second phase of increase is apparent. The decrease in permeability is probably due to structural changes resulting in part from swelling and dispersion of the dry soil upon wetting and in part to dispersion resulting from a decrease in electrolyte content of the soil solution as any salts present are removed in the percolate.

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<sup>4</sup> This investigation is part of a cooperative study of problems relating to water-spreading conducted jointly by the North Kern Water Storage District; the Arvin-Edison Water Storage District; the Division of Irrigation of the Soil Conservation Service, and the U. S. Regional Salinity Laboratory, U. S. Department of Agriculture; the Bureau of Reclamation, U. S. Department of the Interior; and the Division of Water Resources of the State of California.

<sup>5</sup> Christiansen, J. E., and Magistad, O. C. Unpublished report on laboratory phases of cooperative water-spreading study. U. S. Regional Salinity Laboratory. 1944.

*Phase 2.* When soils are wetted from the surface downward, considerable air is entrapped in the pores (1, 10). As the air is dissolved and removed in the percolating water, the permeability gradually increases, attaining a maximum when all or nearly all of the entrapped air is removed. The minimum permeability appears to be the resultant of two opposing phenomena, that is, the forces described for phase 1 tending to reduce permeability from the beginning and the forces of air removal tending to increase permeability.

*Phase 3.* After the maximum is reached, the permeability decreases with time, rather rapidly at first then more slowly until after 2 to 4 weeks the rate is usually but a small portion of its original value. Frequently it has been observed in laboratory tests that the maximum permeability is reached before the last of the entrapped air is removed. This

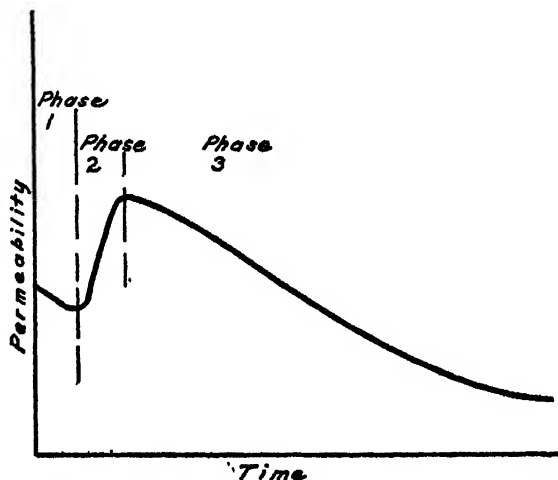


FIG. 1. CHANGES IN PERMEABILITY OF SOILS DURING LONG SUBMERGENCE

suggests that the maximum permeability attained is also the resultant of opposing phenomena. The gradual sealing of the soil during the third phase suggested the following contributing causes:

1. A slow physical disintegration of aggregates under prolonged submergence.
2. Biological clogging of soil pores with microbial cells and their synthesized products, slimes, or polysaccharides (6, 7).
3. A dispersion due to attack of microorganisms on organic materials which bind soil into aggregates (8).
4. A combination of the foregoing factors.

#### EFFECT OF DISINFECTANTS IN WATERS FOR PERMEABILITY TESTS

Christiansen conducted numerous long-time permeability tests<sup>5</sup> in 1943 in which mercuric chloride was added to the local tap water used for the tests. He was able to maintain a considerably higher permeability in all cases with mercury-treated water than with the untreated water. Since mercuric chloride is a strong disinfectant, the results suggested *microbial sealing* as the cause of decreased permeability under prolonged submergence. More recently, additional tests were made by Allison, Martin, and Christiansen<sup>6</sup> on Hesperia soil from San Joaquin Valley and on Hanford loam from near Riverside in which

<sup>5</sup> Unpublished data.

mercuric chloride at various concentrations and other toxic chemicals, chiefly the chlorinated phenols<sup>7</sup>, were added to the water or on the surface of the soil in the case of the insoluble toxics. The specific chemicals and the concentrations used are indicated in table 1. In all these trials a certain measure of success was attained in maintaining high permeability rates. Phenol and formaldehyde at 2000 and 1000 p.p.m. respectively were the most effective treatments. For a considerable time, phenol maintained the permeability at 77 per cent and formaldehyde at 93 per cent of the maximum for the particular soil tested. Eventually, however, the soil sealed up, even with the most effective treatments.

TABLE 1

*Disinfectants added to tap water\* used in permeability tests on disturbed soils*

CHEMICAL	CONCENTRATION
Mercuric chloride.....	20-500 p.p.m.
Phenol.....	50-2000 p.p.m.
Formaldehyde.....	50-1000 p.p.m.
Chloroben.....	100 p.p.m.
Toluene.....	100 p.p.m.
Carbon bisulfide.....	100 p.p.m.
D-D.....	100 p.p.m.
Na-orthophenylphenate (Dowicide A).....	100 and 500 p.p.m.
Na-2,4,5-trichlorophenate (Dowicide B).....	100 and 500 p.p.m.
Na-chloro-2-phenylphenate (Dowicide C).....	100 p.p.m.
Na-2-chloro-4-phenylphenate (Dowicide D).....	100 p.p.m.
Na-2-bromo-4-phenylphenate (Dowicide E).....	100 and 500 p.p.m.
Na-2,3,4,6-tetrachlorophenate (Dowicide F).....	100 and 500 p.p.m.
Na-pentachlorophenate (Dowicide G, or Santobrite).....	100 and 500 p.p.m.
Pentachlorophenol (Dowicide 7, or Santophen 20).....	1 inch layer on soil
Orthophenylphenol (Dowicide 1).....	1 inch layer on soil
2,4,5-trichlorophenol (Dowicide 2).....	1 inch layer on soil

\* Tap water contained 280 p.p.m. of salts and a sodium percentage of 40.

Although permeability tests, in which toxic chemicals were used in the waters, strongly suggested microbial sealing, they failed to present conclusive evidence of this fact. The evidence did not entirely rule out the possibility that physical disintegration of the so-called water-stable aggregates might be a partial cause of decreased permeability under conditions of prolonged submergence. If permeability tests could be conducted under conditions of complete sterility and the maximum permeability was not maintained for a considerable time, then physical breakdown of aggregates would be indicated. To obtain quantitative evidence regarding the exact effect of microorganisms on the permeability of soils under prolonged submergence, permeability tests were made in a sterile system.

<sup>7</sup> The chlorinated phenols were supplied by Monsanto Chemical Co. and Dow Chemical Co.

## SOIL PERMEABILITY UNDER STERILE CONDITIONS

*Methods*

Three soils were selected for comparison in this study: Hanford loam from near Riverside, California, and Exeter and Hesperia sandy loams from Kern County, California, from near the site of water-spreading operations. They were air-dried, passed through a 2-mm. sieve and placed in glass percolation tubes (permeameters) in 100-gm. quantities, according to a standard procedure described elsewhere (1, 2). The soil was compacted to simulate field density by dropping the tube on its point ten times through a distance of 1 inch. The tubes were then covered with small beakers and sterilized in a suitable chamber by the method of Roberts *et al.* (12). This method uses ethylene oxide gas as the sterilizing agent, and for studies involving permeability it has the particular advantage over steam sterilization that it does not appreciably alter the physical and chemical properties of the soil.

The characteristics of the water used in permeability tests are important. Since most tap waters contain some bacteria and traces of soluble organic matter, it was decided to simulate the cation content of the local tap water by adding 1.7 m.e.  $\text{CaCl}_2$ , 0.5 m.e.  $\text{MgCl}_2$ , and 1.5 m.e.  $\text{NaCl}$  per liter to distilled water. Mercuric chloride was also added at the rate of 10 p.p.m. to protect the filters against clogging, and to safeguard the filtered water in case a stray microorganism should pass through the cotton filter on the air-intake tubes of the delivery bottles. This synthetic water was prepared about 10 days in advance of use and stored in 5-gallon bottles. During storage, the mercury destroyed most of the bacteria present in the distilled water and added salts. The water used for the controls and for the reinoculated sterilized soils was not filtered and received no mercuric chloride.

A satisfactory test for sterility of the soils treated with ethylene oxide and for the filtered waters treated with mercuric chloride was obtained by transferring about 0.5 gm. of soil or 2 to 3 ml. of water into standard nutrient broth.

To provide enough sterile water for making several permeability tests simultaneously, the apparatus shown in figure 2 was devised. The various parts of this closed-system were sterilized separately by autoclaving and were connected under aseptic conditions. The system consists of a battery of three auto-irrigator-pots<sup>a</sup> (11) with porous inner walls (fig. 3) serving as filters, an upper reservoir, and a series of four delivery bottles each equipped with Mariotte

<sup>a</sup> Auto-irrigator-pots were obtained from the General Ceramics Co., Refractories Division, New York City. When tested under water at a pressure of 2 atmospheres, it was found that the walls when wet did not leak air. This indicated a maximum pore size of less than 0.75  $\mu$  as determined by the formula:

$$p = \gamma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \text{ or } r = \frac{2\gamma}{p}$$

where  $r_1$  and  $r_2$  = principal radii of curvature;  $\gamma$  = surface tension of water in dynes/cm.;  $p$  = pressure difference in dynes/sq. cm.



siphon tubes to give constant head control in the permeameters, or percolation tubes (fig. 4). The water to be used is placed in bottle *A* from which it automatically siphons over into filter *B*. The water level in the filter is regulated by a

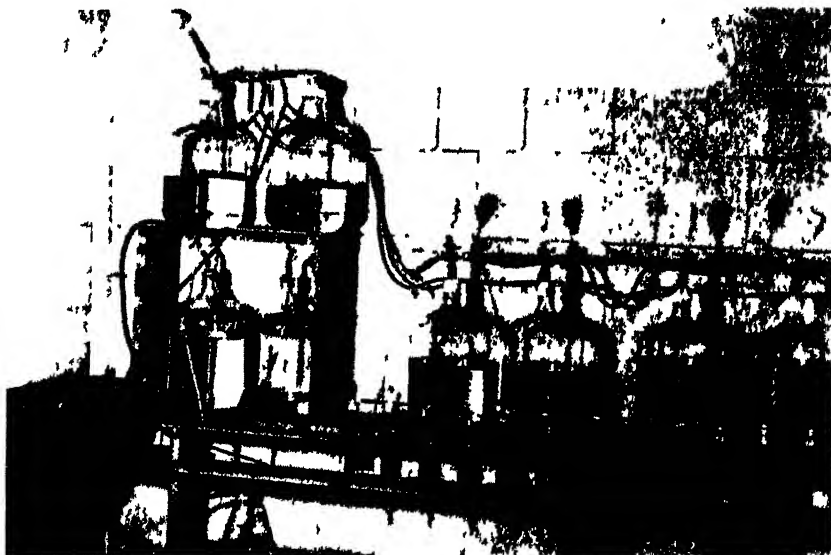


FIG. 2. STERILE CLOSED SYSTEM FOR CONDUCTING PERMEABILITY TESTS ON SOIL UNDER STERILE CONDITIONS

*A*—bottle for supplying water to filter; *B*—filter, *C*—upper reservoir for collecting filtered sterile water, *D*—delivery bottle connected to permeameters below



FIG. 3. FILTER SYSTEM CONSISTING OF DOUBLE-WALLED AUTO-IRRIGATOR-POTS WITH POROUS INNER WALLS, FOR REMOVING MICROORGANISMS

Mariotte siphon tube in bottle *A*. A vacuum (equivalent to a 22-inch mercury column) placed on the upper reservoir, *C*, fills the reservoir by drawing water through the filter, which removes all microorganisms (13). Once the water passes the filter it is sterile and, because it is in a closed system, it is no longer

subject to contamination. The delivery bottles, *D*, are filled individually by gravity flow from reservoir *C* by means of a system of two lines which permits the air from *D* to flow up into *C* as water flows down to *D*. The soils under test are protected from possible disturbance during bottle-filling operations by clamping of the delivery tube at the top of each permeameter unit. The delivery bottles, *D*, are protected with sterile cotton filters so that the air, entering to

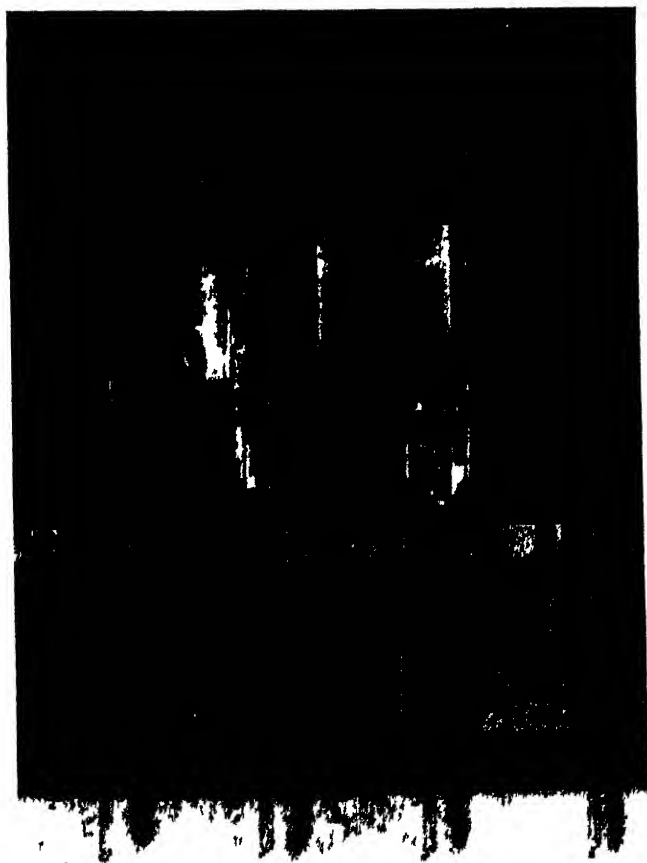


FIG 4 PERMEAMETER UNIT CONSISTING OF FOUR PERCOLATION TUBES  
CONNECTED IN SERIES

replace water used in the tests, is freed of microorganisms. Likewise, a sterile filter is used on reservoir *C* to protect it when the partial vacuum, resulting from filling operations, is released prior to filling of the bottles, *D*.

The permeameters containing the sterile soil were connected to the delivery bottles under aseptic precautions. Water was applied to the permeameters in such a way that disturbance of the soil was avoided. The tests were conducted

in a constant-temperature room kept at 70 to 72° F. The percolate was collected and measured for a definite time period, 15 to 60 minutes, depending on the flow rate. Permeability was calculated (1, 3) by the Darcy equation.<sup>9</sup> As a means of checking on conditions of sterility, the percolate from each permeameter was tested in nutrient broth at the beginning, three times during, and at the end of the experiment. In addition, the soils were removed from the permeameters and sections from the center of the cores were tested in nutrient broth for evidence of growth. All tests were negative, indicating that the major objective was attained, that is, the determination of soil permeability in the absence of microorganisms.

### *Results and discussion*

The results of long-time sterile permeability tests on Hanford loam and on Exeter and Hesperia sandy loams are shown in figures 5, 6, and 7. The curves for the sterile soil receiving sterile water represent two of the four replicates for each which exhibited highest and lowest permeability respectively. Since the other replicates occupied intermediate positions, they are not shown. The control curves shown represent nonsterile and reinoculated sterile soil, respectively, both of which received nonsterile water of similar composition, except that the 10 p.p.m. of mercury was omitted. The permeability values, expressed in centimeters per hour, may be converted to inches per hour by dividing by 2.54, or to feet per day by multiplying by 0.79.

The Hanford soil was included for study because it is a naturally permeable soil which when submerged exhibits quite characteristically all three phases of a typical permeability-time curve (fig. 1). Notably, after reaching its maximum permeability it seals up more readily than most soils. In this test the controls failed to attain a very high maximum as compared to the sterile soil. In explanation of this observation, it must be pointed out that from an initial dry soil condition as in these tests, the permeability reaches its highest point only after the entrapped air is removed from the soil pores by solution in the percolating water (1, 10). Simultaneously, microbial activity begins and soil sealing follows, so that the maximum permeability finally attained is the resultant of two opposite processes. Being fairly rich in organic matter, the Hanford soil has a very active microflora, which causes rapid sealing under continuous submergence. After attaining the maximum permeability, the sterile soil remained highly permeable throughout the test, exhibiting only minor variations with time, whereas both the unsterilized soil and the reinoculated sterile soil sealed readily. After 75 days the sterile soil was as permeable as it was at the end of the 14 days when it reached its highest permeability.

<sup>9</sup> Permeability determinations were made at constant head and calculated according to the transposed Darcy equation:  $P = Q \frac{L}{AH}$  where  $P$  is the Darcy coefficient of permeability,  $Q$  is the flow (volume per unit of time),  $L$  is the length of the soil column,  $A$  is the cross-sectional area of the column, and  $H$  is the difference in head between the two ends of the column.

Even though the Exeter and Hesperia soils are much more permeable than the Hanford soil, they exhibited permeability-time trends which, in general, are very similar to those for the Hanford soil. Because of their very sandy nature they contain large pores, which make for high initial permeability. They contain

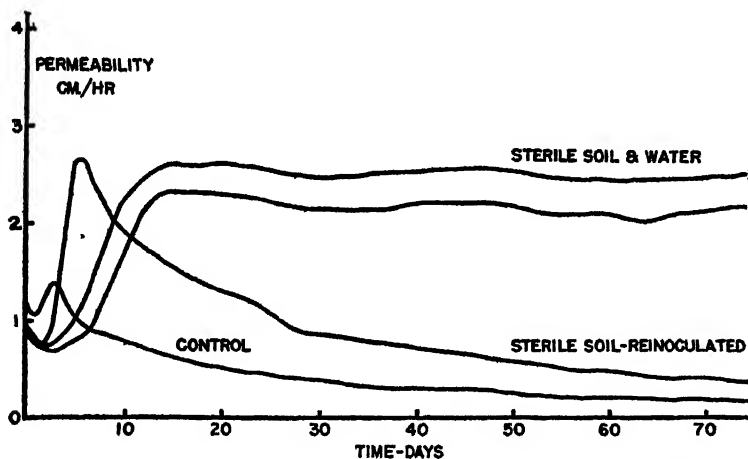


FIG. 5. PERMEABILITY-TIME CURVES FOR HANFORD LOAM UNDER PROLONGED SUBMERGENCE

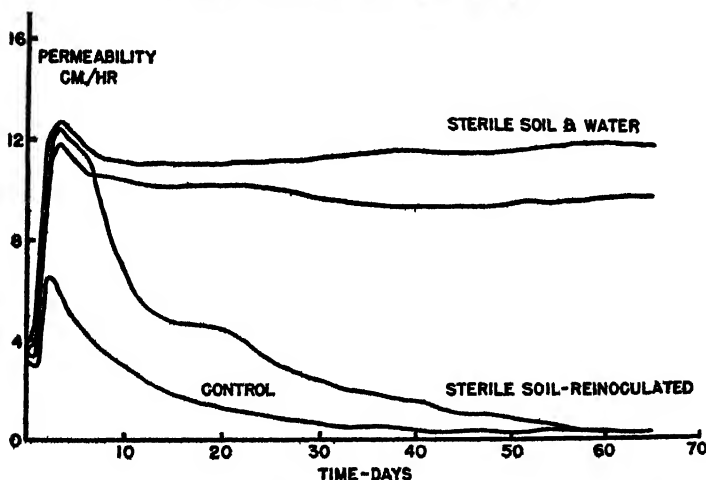


FIG. 6. PERMEABILITY-TIME CURVES FOR EXETER SANDY LOAM UNDER PROLONGED SUBMERGENCE

relatively little organic matter and therefore a less abundant microflora than the Hanford soil. Because of these characteristics they would not be expected to seal up so readily under continued submergence as a soil having smaller pores and a more active microflora.

The significant fact revealed by this investigation is that microbial activity

appears to be the cause of eventual low permeability, or soil-sealing, under conditions of prolonged submergence. Although this evidence was obtained on soils tested under laboratory conditions, there is no apparent reason why this microbial action does not also occur under field conditions of continuous flooding. The data strongly suggest that purely physical disintegration of water-stable aggregates is not responsible for this sealing phenomenon; otherwise, a large reduction in permeability would have occurred in the sterile soils.

Although microorganisms are indicated as the cause of soil-sealing, the exact mechanism involved is still a matter of speculation. Martin (7, 8) found that certain products of microbial growth called "polysaccharides" (often referred to

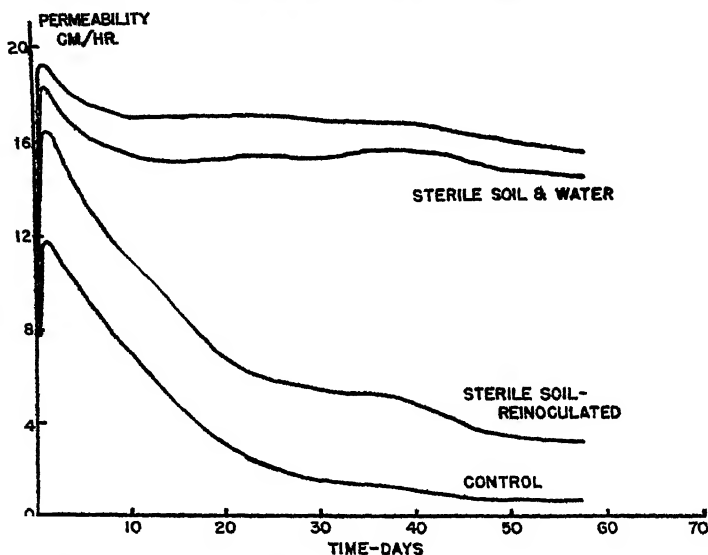


FIG. 7. PERMEABILITY-TIME CURVES FOR HESPERIA SANDY LOAM UNDER PROLONGED SUBMERGENCE

as "mucus-like materials" or "gums") have strong aggregating influence when soils containing them are subjected to drying. He also found that the production of aggregating substances in soils is greatly stimulated by the addition of an energy material such as sucrose or dextrose and by incubation for a time. Previous studies at this laboratory indicated that when sucrose is added to water used in long-time permeability tests the soil seals up completely within 2 days, whereas if no soluble energy material is added, the sealing is always much slower. In either case, if the sealed soils are air-dried, sieved, and retested, the initial and maximum permeabilities on second test are always appreciably higher for the untreated soil and very much higher for the sucrose-treated soil, which sealed up most rapidly in the original test. If it is assumed that the higher permeability obtained on retest of the sealed soil is due to improved aggregation as a result of drying, then it appears that the microorganisms, which cause the soil to seal when continuously submerged, are capable of producing soil-aggregat-

ing substances such as polysaccharides even in the absence of added energy materials. There seems to be no other plausible explanation for increased permeability on retest of previously sealed soils which received no soluble energy additions.

Martin (7) added bacterial polysaccharides to soil and, after drying and re-moistening, studied the persistence of the aggregating material with time. From this study he concluded that, "the substance [polysaccharide] is readily destroyed by certain members of the soil population." In reference to the mechanism of soil-sealing it might be reasoned that under prolonged submergence the decrease in permeability that eventually occurs may be attributed in part to a dispersion of aggregates due to microbial attack on the substances that bind soil particles together. The major cause, however, is attributed to the clogging of pores by the currently produced products of microbial activity.

The process of microbial soil-sealing appears to occur in the following cases:

- (a) In water spreading on permeable agricultural soils.
- (b) During prolonged leaching operations to remove alkali salts.
- (c) In cropping practices such as rice growing—the sealing which takes place during prolonged submergence probably contributes to the economy of water utilization during the flooding period and also to a favorable permeability of the soil after it dries out.

#### SUMMARY

The permeability of continuously submerged soils usually decreases slightly at first and then increases appreciably as the entrapped air is removed by solution in the percolate. Subsequently, a large reduction in permeability occurs until the soil virtually seals up.

Sterile permeability tests conducted to determine the cause of decreased permeability under prolonged submergence gave no evidence of soil aggregate breakdown due to purely physical causes. The reduced permeability appears to be due entirely to microbial sealing. The soil pores probably become clogged with the products of growth, cells, slimes, or polysaccharides. If any of the observed reduction in permeability was due in part to disintegration of soil aggregates, the dispersion is believed to be due to biological causes, that is, the attack of microorganisms on the organic materials which bind soil into aggregates.

Soils may be readily sterilized in the laboratory with ethylene oxide gas without appreciable change in their physical properties. For certain research purposes, this method offers advantages over that of steam sterilization.

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# A CONVENIENT METHOD FOR ESTIMATING CARBONATES IN SOILS AND RELATED MATERIALS<sup>1</sup>

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The use of an alkalimeter provides the most convenient method of estimating carbonates in soils and related materials high in that constituent. In using an alkalimeter, however, it is necessary to decompose all carbonates and expel CO<sub>2</sub>, at the same time avoiding the loss of volatile substances other than carbonate-derived CO<sub>2</sub>. To accomplish this, when applied to soil materials, the acid used to liberate the CO<sub>2</sub> from the carbonate must meet the following requirements:

1. The degree of ionization must be high enough to decompose the most resistant carbonates.
2. It must have a low vapor pressure at room temperatures and pressures.
3. It must not oxidize organic compounds.
4. It must not reduce MnO<sub>2</sub> to give volatile substances.

Trichloroacetic acid meets the foregoing requirements. It is a crystalline solid which melts at 57.5°C., boils at 195.3°C., and is extremely soluble in water (15 gm. of acid to 1 ml. of water). This water solution has a pK value of 0.7 giving a calculated hydrogen-ion concentration of 1.24 gm. per liter, which is equivalent to the hydrogen-ion concentration of 1:10 HCl commonly used to liberate CO<sub>2</sub> in carbonate estimations. Trichloroacetic acid is not an oxidizing agent, and it was found to give no volatile substances when 25 ml. of 15:1 acid was mixed with 10 gm. of MnO<sub>2</sub> for 16 hours at 27°C. Consequently, the present method was developed using trichloroacetic acid to obviate the difficulties encountered when the more common strong mineral acids are used in an alkalimeter to liberate carbonate CO<sub>2</sub>.

## APPARATUS

Any of the many alkalimeters mentioned by Treadwell and Hall<sup>3</sup> can be adapted for use with this method, or a simple alkalimeter, shown in figure 1, may be made from apparatus commonly found in any laboratory. The reaction flask is a 50-ml. Erlenmeyer flask (*f*) which has a short 5-ml. pyrex test tube (*t*)

<sup>1</sup> Contribution from the department of agronomy, University of Illinois Agricultural Experiment Station. Published with the approval of the director of the Illinois Agricultural Experiment Station.

<sup>2</sup> First assistant in soil survey; formerly graduate student department of agronomy, University of Illinois, and now professor of soil science, National Peking University, Peiping, China; professor in soil physics, respectively. The writers are indebted to R. S. Smith for his interest and cooperation in this study.

<sup>3</sup> Treadwell, F. P., and Hall, W. T. 1924 Analytical Chemistry, vol. 2, ed. 6, p. 331. John Wiley & Sons, Inc., New York.



fused to the inside wall. The flask is fitted with a No. 2 two-hole rubber stopper. An absorption tube (*a*) may be made from one half of a Schwartz ground-glass-stoppered U-tube. This absorption tube is inserted in one hole of the rubber stopper, and a glass tube attached to a small ground glass stopcock (*S*<sub>2</sub>) is inserted in the other hole of the stopper.

#### PROCEDURE

A 2-gm. sample of 100-mesh soil (or an amount equivalent to less than 0.25 gm. of  $\text{CaCO}_3$ ) is placed in the reaction flask of the alkalimeter, care being taken to ensure that no part of the sample falls in the test tube within the flask. One milliliter of water is added to the sample and 5 ml. of a mixture of trichloroacetic

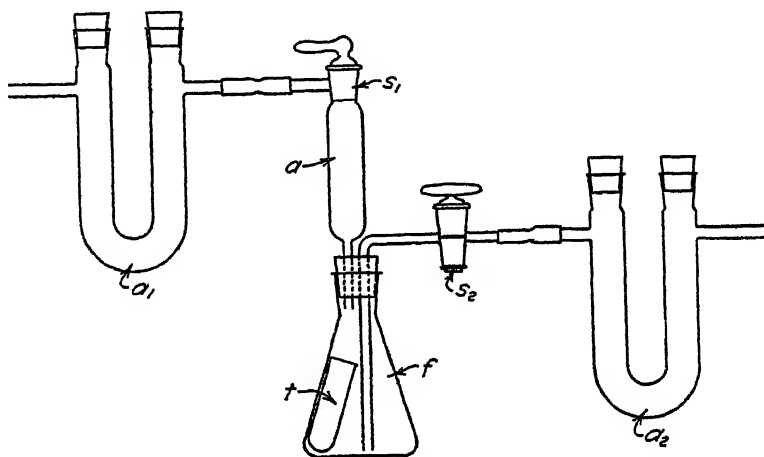


FIG. 1. DIAGRAMMATIC SKETCH OF ALKALIMETER USED IN CARBONATE ESTIMATIONS

acid and water (15 gm. of trichloroacetic acid and 1 ml. of water) is introduced into the test tube within the flask. Here again care must be exercised to avoid mixing the acid with the soil sample at this time. The absorption tube (*a*), in the two-holed rubber stopper, is filled with magnesium perchlorate (Anhydrone) and covered with a cotton plug. The rubber stopper is inserted in the reaction flask, the stopcocks are closed, and the alkalimeter is weighed. The alkalimeter is then protected from atmospheric moisture by means of two U-tubes (*a*<sub>1</sub> and *a*<sub>2</sub>) containing Anhydrone. Stopcock *S*<sub>1</sub> is opened and the trichloroacetic acid is mixed with the soil sample by tilting and swirling the alkalimeter. After 12 hours the reaction will be complete. When this is accomplished stopcock *S*<sub>2</sub> is opened and the remaining  $\text{CO}_2$  in the alkalimeter is displaced by air drawn slowly through the alkalimeter for 10 minutes. The stopcocks *S*<sub>1</sub> and *S*<sub>2</sub> on the alkalimeter are closed and the U-tubes *a*<sub>1</sub> and *a*<sub>2</sub> are detached. The alkalimeter is then weighed. The difference between the weight of the alkalimeter before and after the reaction represents the weight of  $\text{CO}_2$  liberated from the carbonates in the soil sample.

TABLE 1

*Comparison of the trichloroacetic acid method with standard methods\* of determining calcium carbonate equivalent*

METHOD	CaCO <sub>2</sub> EQUIVALENT		
	Dolomite	Calcite	Loess
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Trichloroacetic acid method.....	106.2	98.4	6.1
Neutralization of H <sub>2</sub> SO <sub>4</sub> .....	107.3	98.7	...
Neutralization of HCl.....	104.7	....	...
Muffle furnace 1050°C.....	107.3	98.4	...
Carbon train 1050°C.....	106.0	98.4	6.0
A.O.A.C. 1 hour.....	96.7	....	6.2
A.O.A.C. 2 hour.....	106.0	....	...

\* Association of Official Agricultural Chemists 1940 Official and Tentative Methods of Analysis, ed. 5. Washington, D. C.

Winters, E., and Smith, R. S. 1929 Determination of total carbon in soils. *Indus. and Engin. Chem., Analyt. Ed.* 1: 202-203.

TABLE 2

*Comparison of the trichloroacetic acid method and the A.O.A.C. method for estimating calcium carbonate equivalent in calcareous loess*

CaCO <sub>3</sub> EQUIVALENT					
SAMPLE NUMBER	Triplicate analyses				A.O.A.C.
	I	II	III	Average	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
1620	6.1	6.0	6.1	6.1	6.2
b748	17.2	16.9	17.1	17.1	16.8
b810	12.6	12.5	12.6	12.6	12.6
b81	42.7	44.1	43.3	43.4	40.8
A817*	3.5	3.7	3.6	3.6	3.4

\* Buried surface soil.

TABLE 3

*Recovery of carbonate CO<sub>2</sub> from known mixtures by the trichloroacetic acid method*

SAMPLE	AMOUNT CARBONATE CO <sub>2</sub> ADDED	AMOUNT CARBONATE CO <sub>2</sub> RECOVERED
	<i>gm.</i>	<i>gm.</i>
1.5 gm. of Drummer clay loam	None	0.0013
1.5 gm. of Drummer clay loam + 0.5 gm. of dolomite	0.2320	0.2332
2.0 gm. of muck	None	0.0023
2.0 gm. of muck + 0.5 gm. of dolomite	0.2320	0.2320

#### EXPERIMENTAL RESULTS

The trichloroacetic acid method was used to estimate the carbonate equivalent of dolomite, calcite, and calcareous loess. The carbonate equivalent of replicate

samples was estimated by several methods commonly used for this purpose. A comparison of the data from these methods is given in tables 1 and 2.

The method was given a rigorous test by CO<sub>2</sub> recovery estimations on standardized dolomite samples mixed with soils containing large amounts of organic matter. Accurate recovery of CO<sub>2</sub> in mixtures of this type was expected to be difficult because of the large proportion of dolomite to trichloroacetic acid and of the tendency of certain components of soil organic matter (that is, compounds in which a carboxyl group is attached to an active methylene group) to release CO<sub>2</sub> when treated with acids. Samples for these recovery studies were prepared by mixing known amounts of standardized dolomite with carbonate-free muck and surface samples of carbonate-free Drummer clay loam (a black clay loam). The results are reported in table 3.

#### CONCLUSIONS

The results obtained in this study justify the following conclusions:

The use of trichloroacetic acid in a loss-of-weight alkalimeter method gives results equal in reliability to the methods commonly used for carbonate estimations in soils, limestone, etc.

Satisfactory recovery of CO<sub>2</sub> was obtained on known amounts of standardized dolomite when mixed with large quantities of carbonate-free soils containing a high content of organic matter.

The proposed method offers distinct advantages over other methods for the estimation of carbonates in soils. It is simple, convenient, and may be time-saving. Though a long time is needed for the complete release of CO<sub>2</sub> from resistant carbonates, the attention of the analyst is not required during this period.

# IMPROVEMENTS IN THE PLASTER OF PARIS ABSORPTION BLOCK ELECTRICAL RESISTANCE METHOD FOR MEASURING SOIL MOISTURE UNDER FIELD CONDITIONS<sup>1</sup>

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Since its introduction in 1940, the plaster of paris block method of measuring soil moisture by means of electrical resistance (4) has been widely employed in agricultural fields. Hydrologic research<sup>2</sup> (13), war production problems involving guayule culture (8, 9), and many other investigations ranging from field irrigation to greenhouse studies have made use of this technique.

Briefly, the method consists of imbedding within the soil a plaster of paris block containing two electrodes. At a constant temperature, the electrical resistance of the plaster of paris varies with its moisture content, which, in turn, varies according to the magnitude of the forces exerted by the surrounding soil. A determination of the block resistance thus gives a measure of these soil moisture forces—a measurement which can be made with a high degree of accuracy and reproducibility within the soil moisture range that is of significant importance to growing plants (9).

## FUNDAMENTAL PRINCIPLES

Because the plaster of paris absorption block indicates the force with which moisture is held by the soil environment, it may be considered to portray more accurately than conventional volume or weight percentages soil moisture conditions as they exist with respect to actively transpiring plants. The conventional percentages have, of course, long been recognized as inherently fallacious in this regard because they cannot express free energy factors operating in moisture phenomena.

Figure 1 is a typical curve based on several measurements of the *soil moisture-block resistance* relationship. It illustrates that the absorption block may offer at least a partial solution to soil water problems. Other investigators (1, 5, 7, 8, 10, 13) have confirmed the shape and general characteristics of this curve, which, it is interesting to note, exhibits a marked resemblance to the moisture stress-soil moisture curves recently developed by Wadleigh (12). This resemblance confirms the fundamental nature of the absorption block technique.

Unique features of the absorption block are that (a) the relationship between moisture in the soil and block resistance is basically one of free energy and (b) the measurable range of sensitivity coincides with the critical variation of soil

<sup>1</sup> Authorized by the director for publication as journal article No. 850 (N. S.) of the Michigan Agricultural Experiment Station.

<sup>2</sup> Garstka, W. U. Unpublished data. Michigan Hydrologic Research Project, Soil Conservation Service, U. S. Department of Agriculture.

water. In other words, the range of the technique corresponds with the quantity of moisture between the permanent wilting point and approximately the moisture equivalent. In terms of the absorption block technique, this *available* water is the water held in the soil by forces of such low magnitude that the block resistance is less than the asymptotic value which the curve approaches with respect to the moisture index. An arbitrary average resistance of 75,000 ohms has proved practical as an indicator of the maximum forces against which plants can obtain moisture from the soil (table 1). Further, more fundamental studies,

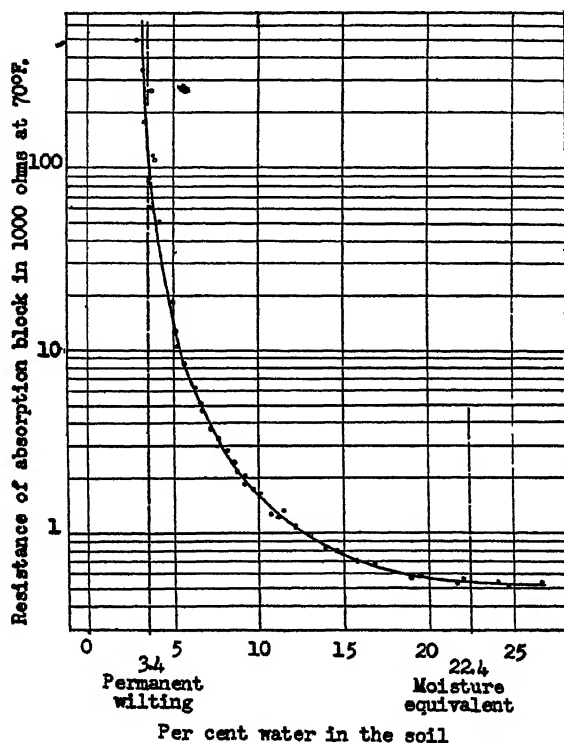


FIG. 1. ABSORPTION BLOCK RESISTANCE AS A MEASURE OF SOIL MOISTURE

may reveal that a resistance of a somewhat higher order, perhaps in the vicinity of 1,000,000 ohms, is a better index. The steep gradient of that portion of the curve in question means that exceedingly small changes in the volume of total soil water give rise to relatively great resistance changes. These are of little practical significance, however, because of the small moisture volume changes. Moreover, it is a generally accepted concept that the wilting point (by virtue of its definition) is a narrow range rather than a specific value (6, 11), and therefore an arbitrary resistance value becomes a practical necessity.

On the other extreme, when the curve becomes asymptotic with respect to resistance, that is, when block resistances fall to a minimum constant level, the soil contains abundant moisture and is perhaps losing some water in response to

gravitational forces. Here again, experience has indicated that a convenient, although arbitrary, critical minimum value is about 600 ohms (table 2). Rising

TABLE 1

*Permanent wilting point of various soil samples as indicated by the electrical resistance of standard plaster of paris absorption blocks*

All values in terms of oven-dry weights

SOIL DESCRIPTION	PERMANENT WILTING BY DILATOMETER METHOD (3)	WATER REMAINING IN SOIL AT BLOCK RESISTANCE OF 75,000 OHMS
	<i>per cent</i>	<i>per cent</i>
Hillsdale sandy loam, surface.....	4.7	4.5
Grundy silt loam, surface.....	12.5	13.0
Clinton silt loam, surface.....	6.5	6.2
Shelby silt loam, surface.....	12.3	12.5
Davidson clay loam, surface.....	14.4	12.5
Altamont adobe, surface.....	14.7	15.3
Clyde loam, surface.....	26.0	26.0
Sierra Nevada sandy loam.....	6.7	6.2
Antioch clay loam, surface.....	6.6	6.6
Palouse silt loam, surface.....	11.7	11.7
Brookston silt loam, surface.....	14.3	13.6
Vina loam, surface.....	13.8	13.6
Putnum silt loam, surface.....	10.8	12.8
Aitken clay loam, surface.....	18.6	18.7
Hawaii clay, surface.....	23.4	23.5
Purdue clay, surface.....	15.3	17.0
Ontonagon clay, B horizon.....	18.4	16.0
Hillsdale sandy loam, subsurface.....	10.8	10.4
Miami silt loam, B horizon.....	13.8	15.2

TABLE 2

*Moisture equivalent of various soil samples as indicated by the electrical resistance of standard plaster of paris absorption blocks*

All values in terms of oven-dry weights

SOIL DESCRIPTION	MOISTURE EQUIVALENT BY SUCTION METHOD (2)	WATER REMAINING IN SOIL WHEN RESISTANCE BEGINS TO INCREASE*
	<i>per cent</i>	<i>per cent</i>
Janesville silt loam, surface.....	23.7	24.0
Shelby silt loam, surface.....	30.1	32.0
Coloma sand, surface.....	9.6	10.7
Grundy silt loam, surface.....	28.4	28.7
Miami silt loam, surface.....	12.6	13.8
Hillsdale sandy loam, surface.....	24.7	25.5
Rubicon sand, subsoil.....	9.7	10.9
Ontonagon clay, B horizon.....	38.5	35.2

\* Generally in the vicinity of 450 to 650 ohms.

resistance values indicate that the available soil moisture is decreasing and that the portion remaining in the soil is being held with correspondingly greater forces.

Tables 1 and 2 reveal that an arbitrary resistance value of about 75,000 ohms characterizes the permanent wilting point of a fairly large member of widely different soil samples, whereas resistance values of 450 to 650 ohms characterize the moisture equivalents. This evidence suggests that, for practical purposes, these resistance values will characterize the respective extremes of moisture status for *all* soils (except where high salt concentration, and thus high osmotic potentials, are encountered). The validity of these relationships is confirmed by present information which seems to indicate that the soil moisture potential is

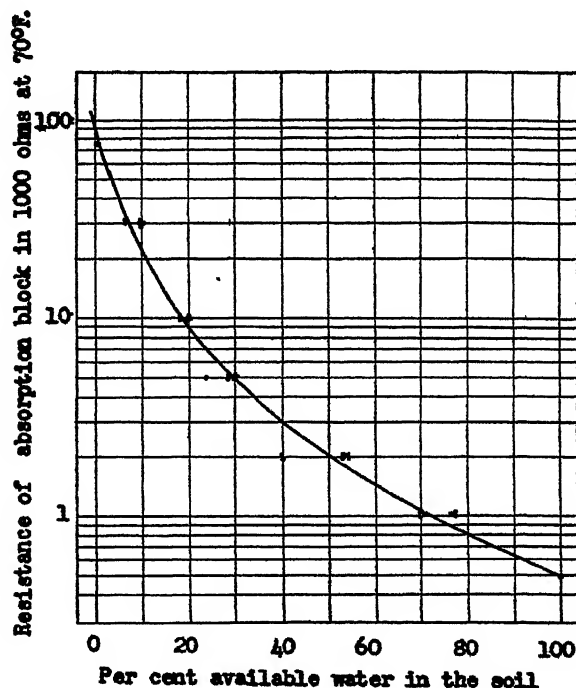


FIG. 2. ABSORPTION BLOCK RESISTANCE AS AN INDICATOR OF AVAILABLE SOIL WATER

The six determinations in each group of coordinates are values obtained in samples of Brookston clay loam, Miami silt loam, Conover loam, Hillsdale sandy loam, Brady sandy loam, and Berrien loamy sand.

about the same for all soils when they are at their permanent wilting percentage or at their moisture equivalent percentage (11).

Figure 2 illustrates the nature of the curve between these two extremes, the end points being established by tables 1 and 2. The horizontal scale represents the difference between the permanent wilting percentage and the moisture equivalent percentage; this is the range of so-called available water. Soil moisture has been reduced on an oven-dry basis to "per cent available water," which is plotted against block resistances. The midpoint of the horizontal scale represents soil conditions when approximately 50 per cent available water is present;

these conditions, for practical purposes, correspond to block resistances of about 2000 ohms. Other block resistance values may similarly be converted into corresponding available water percentages. This feature of the absorption block technique is thought to possess great practical implications, since it eliminates the necessity for calibrating the instrument except for the most exacting applications.

A more accurate and more fundamental concept is that for any given resistance, different soils hold water with approximately the same force, a statement which is comparatively exact when limited to the *drying* portion of the soil water fluctuation cycle. It is this part of the cycle that is of primary interest in forecasting the water requirements of crops. It is because of hysteresis exhibited between drying and wetting tension curves, because at any given moisture content different soils do not exhibit the same pressure deficiencies, and because of osmotic differences that an apparent variation is encountered in any attempt to correlate thermodynamic measurements with more or less empirical constants. Statistical significance cannot be expected to obtain, at least not to a high degree, between such attributes. Nor is a high degree of significance necessary, because the moisture constants are of little value in actual field management practices. Despite their inherent inadequacies, however, the constants are here employed to facilitate the presentation of this technique, because they are familiar terms, and because they have been widely, although often erroneously, used.

From a practical viewpoint, then, the generalized curve can be advantageously used to predict the most economical time to supply water to growing plants. Experience in Michigan has indicated that this time is reached when the block resistance approaches or slightly exceeds 10,000 ohms. The minimum level of the curve is also of importance, since it indicates how much water can be economically supplied without great drainage losses. Continued resistance readings of about 600 ohms mean that excess water is present. Additional supply may not only be costly but it may also decrease aeration. It is thus seen that for utilitarian field uses, standard, uniform resistance blocks need not be calibrated, since the shape and critical portions of the block resistance soil moisture curve are already revealed. Supplementary soil temperatures may or may not be necessary, depending on the particular problem at hand. As the relatively narrow range of soil temperature fluctuations during the Michigan growing season is not considered to result in appreciable error in field studies, block resistances are seldom corrected to a uniform temperature.

Detailed studies may be accomplished by calibrating block resistances against soil moisture, correcting all measurements to a standard temperature. Other investigators (7) have perfected a fairly rapid and satisfactory calibration technique which enlarges the scope of this method, adapting it to many agricultural, industrial, and even fundamental research studies involving soil moisture forces, stresses, flows, and also volume and mass relationships. It is emphasized, however, that calibration is not necessary to the use of the standard block resistance as an indicator of the force with which moisture is held by the soil, or as an indicator of approximate volume and mass relationships, that is, the amount of available water present in the soil.



Enhancing the value of the plaster of paris block as a soil moisture indicator for use in large-scale installations are the following advantages:

1. After the initial installation, which is relatively simple, the soil need not be disturbed.
2. Readings may be made by unskilled labor.
3. Single readings require a minimum of time, generally not in excess of 1 minute; several hundred readings can be made by a single operator in the course of a working day.
4. The blocks may be completely buried so that their presence does not interfere with surface tillage or plant growth or in any other way with crop production.
5. The plaster of paris units are not costly; this, together with the ease of obtaining individual measurements, makes feasible a large number of replications.

Another advantage of this plaster of paris method is that it gives an indication of the time at which soil freezes, a factor that is sometimes of interest in hydrologic investigations (13). Freezing within the soil mass is indicated by an abrupt rise in the resistance of the block, caused by a sharp decrease in conductivity of the block as the moisture within it changes from the liquid to the solid state. This transition point cannot be obtained by the use of thermometers, since temperatures considerably below the freezing point may not result in freezing within the soil.

#### ABSORPTION BLOCK

Because of the demonstrated usefulness of the method, efforts have been made to improve its accuracy and its ease of manipulation in the field. An extensive search has been conducted to find absorbent materials with energy characteristics and physical properties superior to those of plaster of paris. A large number of substances, including fired clay, various cement and concrete mixtures, dental stones, and a specially designed asbestos board have been tested. Among the plastics investigated were nylon fabrics, glass cloth, and other fibrous materials. In addition, a specially designed bare electrode was examined. A comparison of the results of these electrode units will form the subject matter of a separate paper.

Many varieties of material are marketed as plaster of paris. Differences in both the physical and chemical characteristics of these materials are caused by the varying quantities of *hasteners* or *retarders* which are added to control setting speeds and otherwise standardize a given product for commercial and technical uses. In general, these regulating agents have an unfavorable influence on the soil water-resistance relationships of the blocks; chemically pure materials exhibit a wider range of resistance change for a given change in soil moisture and therefore contribute to the sensitivity of the method. Pure gypsum<sup>3</sup> has proved extremely durable and the best material so far investigated. It sets in about 30 minutes and exhibits a very porous, although relatively soft, structure.

Two materials of a somewhat similar nature, marketed as *Hydrostone* and *Hydrocal*, have been used, because of their extreme hardness, by several investigators. It was thought that this hardness might indicate greater durability

<sup>3</sup> Sold by the United States Gypsum Company as No. 1 White Molding Plaster of Paris.

and that blocks made of hard materials would last longer within the soil. Experience with these materials has shown, however, that their extremely high density is complemented by a very low porosity which reduces not only the relative proportion of water that can be absorbed but also the speed with which it moves within the block and between the block and the soil. The sensitive range of these blocks is narrow, possibly because of their narrow pore-size distribution characteristics. A third objection is the low solubility of these hard materials, which reduces the buffer capacity of the block with respect to salt concentration changes within the soil solution.

Under Michigan climatic conditions, plaster of paris blocks have functioned satisfactorily in well-drained soil profiles for as long as 5 years. On the other extreme, waterlogged conditions encountered in low topographic positions reduce the useful life of the blocks to a single growing season; this is particularly true in organic soils where the blocks dissolve rather rapidly. In intermediate drainage positions, the useful life of the block appears to be determined by the relative length of time it is exposed to saturated conditions. In general, the higher and drier the position of the block, the longer it will function. Freezing conditions do not appear to deteriorate the blocks as rapidly as does solution; blocks show considerable physical disintegration, especially at the corners, after exposure to repeated freezing and thawing, but this superficial disintegration has little effect on the resistance characteristics of the block, until the volume between the electrodes has been substantially reduced.

Investigations concerning the design of the absorption block have led to the conclusion that the original specifications are indeed practical, although perhaps not so theoretically sound as, for example, a coaxial design. Studies of cylindrical blocks containing concentrically arranged electrodes showed that the effects of external electrical fields were minimized. Difficulties were encountered, however, in casting such blocks with a high degree of uniformity. The relative simplicity of the present rectangular pattern and the ease and cheapness with which the blocks can be manufactured appear to offset any theoretical advantages of a coaxial absorption unit. Large quantities of commercially manufactured blocks made according to the original specifications (4) include an average of two defective units in every hundred. A convenient test for uniformity is to measure the resistance of saturated blocks when immersed in distilled water. Resistances between 450 and 410 ohms at 70°F. are considered satisfactory.

#### IMPROVED BRIDGE

A major obstacle in the development of a practical procedure for use in the field was the lack of a sturdy, self-contained, and sufficiently sensitive resistance measuring device. Commercial resistance meters already on the market possessed many disadvantages, chief among which were a limited range, delicate construction, bulkiness, and high cost. In order to overcome these obstacles and to benefit from recent technological developments in the electrical engineering field it was found necessary to design and construct a special resistance measuring device, which has since been considerably improved as a result of wider use and continued experience with the resistance blocks.

As now manufactured<sup>4</sup>, this improved bridge combines rugged, compact construction with a high degree of sensitivity. It is a completely self-contained unit (figs. 3 and 4) which is designed to measure resistances in circuits containing appreciable capacitance, such as is encountered in installations where the blocks may be connected by up to 200 feet of commercial multiple-strand, rubber-coated copper wires.

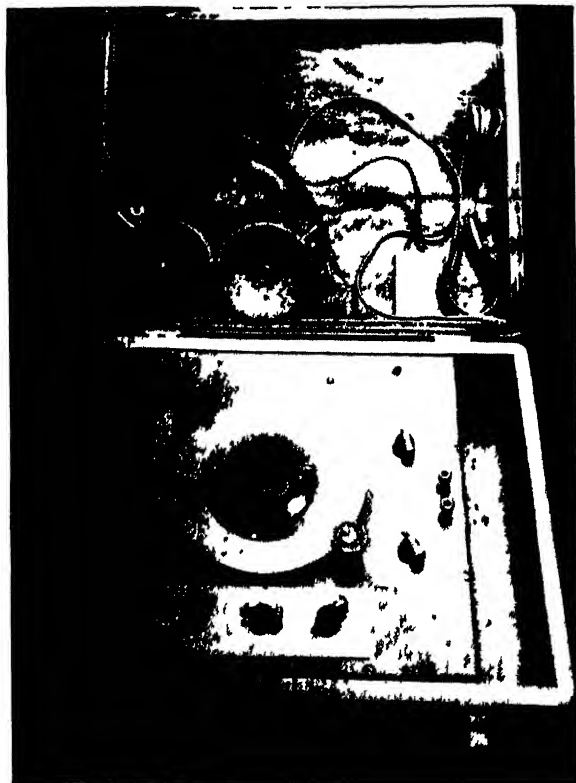


FIG. 3 IMPROVED BRIDGE FOR MEASURING RESISTANCE OF PLASTER OF PARIS BLOCKS

Note that the unit is self-contained, that all circuits are fully covered, and that the earphones are fitted with sponge rubber pads.

Experience with many designs indicated that a wooden case contributes to the effective shielding of the instrument from ground currents, a factor in metal-cased instruments that invariably causes difficulties under certain combinations of circumstances frequently encountered in the field. Headphones are greatly preferred to an "electric eye" indicator. The electric eye, although a satisfactory

<sup>4</sup> The authors wish to acknowledge the services of J. P. Davenport, who assisted in designing the resistance bridge and who is now producing such bridges commercially for the Wood and Metal Products Company, of Bloomfield Hills, Michigan

*null* indicator in the laboratory, is difficult to read under field light unless a shadowbox or curtain is used. This increases the bulkiness of the instrument and adds to the difficulties of manipulation. Galvanometers, likewise, proved unsatisfactory for general field use, inexpensive commercial models being too delicate or else, on the other extreme, lacking in sensitivity. A relatively inexpensive headphone set, however, has proved durable and efficient for general outdoor use. Making use of the sound characteristics of the necessary oscillating current, headphones have proved to be the most useful type of *null* indicator. In conjunction with the present circuit design, a great contrast in tone volume, which rapidly fades to a minimum level within an extremely narrow range, contributes to the ease of adjusting the instrument. For prolonged operation, sponge rubber

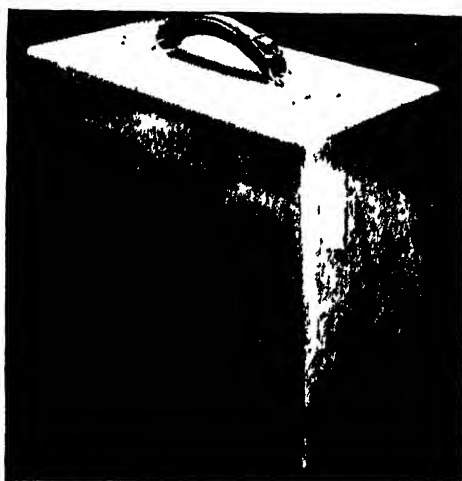


FIG. 4. THE ENTIRE RESISTANCE BRIDGE, INCLUDING POWER PACK, IS CONTAINED IN THIS CASE, WHICH IS HERE CLOSED TO SHOW ITS COMPACTNESS

With batteries the unit weighs about 20 pounds.

cushions over the phones have been found to be helpful by reducing the interference of extraneous sounds such as are produced by wind currents. They also distribute the mechanical pressure over the entire ear cartilage, which adds to the comfort of the operator.

A generalized diagram (fig. 5) of the improved bridge illustrates that the circuits are based on the Wheatstone principle. To avoid the influence of various capacitance factors present in field circuits, a large condenser has been included which contributes greatly in obtaining a good null balance within the bridge. The instrument is powered by dry-cell batteries feeding through a 2000-cycle electronic oscillator. An extremely wide range of sensitivity is obtained by inserting two series of standardized resistances in opposite arms of the bridge; the proper combination is selected by means of multiplier switches, and the final null-point is obtained by adjusting a logarithmic potentiometric

rheostat fitted with a 6-inch graduated dial. The bridge is thus balanced, or tuned to the null point, by manipulating five dials in a matter of seconds. Null adjustments are reduced to the width of not more than two turns of the rheostat coil, which permits finer tuning than can be conveniently interpolated from the graduations.

Compared with general purpose conductivity bridges which are standard items of equipment in most research laboratories, this special bridge has several advantages: it is self-contained and portable; the power unit is rugged enough to withstand shocks encountered in field work; and a sharp null-point is obtainable as a result of including the variable condenser in one of the bridge arms. Compared with the special bridge originally designed for this work, the newer modi-

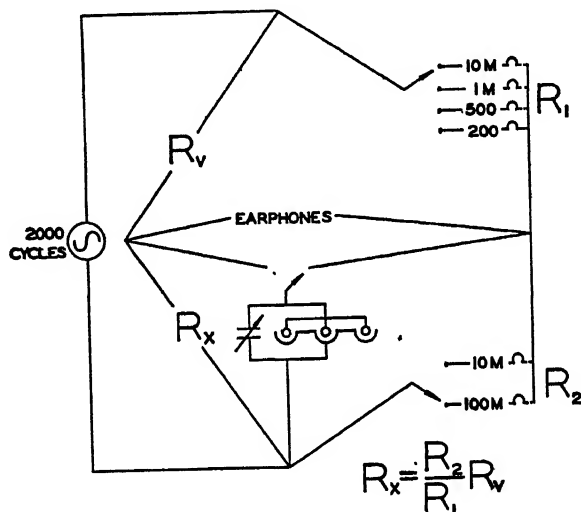


FIG. 5. CIRCUIT DIAGRAM OF IMPROVED BRIDGE

fication has a much wider range: 5,000,000 ohms as against 100,000 ohms for the old model. The oscillator has also been improved, the new model having a much higher power output at a frequency of 2000 cycles. The high power output produces a loud signal that facilitates adjustment because of its great contrast with the null balance, which is, under most conditions, marked by total silence.

An ohm-meter modification of this circuit has been successfully used for several seasons to control irrigation on experimental fields. When the absorption block leads are plugged into this moisture meter, movement of a needle across the dial indicates the extent to which soil moisture has been depleted.

#### SUMMARY

The electrical resistance technique of obtaining a continuous measure of soil moisture *in situ* under field conditions by means of a plaster of paris absorption block is discussed in the light of additional knowledge and experience gained since the inception of the method in 1940.

Fundamental considerations of the characteristics of this technique reveal that for most practical purposes standard absorption blocks need not be calibrated. Resistance readings may be directly interpreted in terms of *available* soil water; in all soils the percentage of available water is approximately the same for any given resistance value.

The maximum longevity of absorption blocks operating continuously in the field may exceed 5 years in a relatively dry environment. A minimum life of one season is found in waterlogged organic soils.

The special resistance bridge has been improved, and a new commercial model is presented and described.

The advantages of the method are summarized.

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# INFLUENCE OF LIME ON THE SOLUBILITY OF POTASSIUM IN SOILS AND ON ITS AVAILABILITY TO PLANTS<sup>1</sup>

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The lime-potash problem is increasing in economic importance in the southeastern United States as the native soil K is depleted by intensive cropping and as increased amounts of lime are used. In 1938, the farmers of Alabama applied directly to the land only 8,500 tons of limestone as such (this does not include liming material added in mixed fertilizers), as contrasted to 270,300 tons in 1944. In spite of this increase, the present consumption of liming materials in the state is relatively small compared with that of most of the states east of the Mississippi River. Even further increases are indicated as farming practices are changed to include more improved pastures and winter legumes.

Rogers (14) found unmistakable evidence that the use of lime increased the K requirements of certain crops on some of the more extensive soils of Alabama.

The literature reveals many conflicting opinions as to what will be the ultimate effect of liming on the availability of soil K. For example, Jenny and Shade (7) reported that the addition of  $\text{CaCO}_3$  liberated large amounts of K on every soil studied, whereas Dean (3), working with Iowa soils, reported that lime did not liberate soil K. Dean said further that Ca may be so active in depressing the solubility of K that in time the soil may become deficient in available K. Peech and Bradfield (10), working with Miami colloidal clay, found no evidence of K fixation regardless of the degree of Ca saturation, whereas Volk (17) and Harris (4) have shown that additions of lime increased the fixation of K.

Extensive reviews dealing with the influence of Ca on soil K and on the absorption of K by plants have been prepared by Peech and Bradfield (11) and by Pierre and Bower (12). Pierre and Bower, summarizing numerous investigations, concluded that "potassium absorption by plants is usually decreased by the presence of high concentrations of cations in solution. Under certain conditions, however, it may be increased."

The investigation reported herein was undertaken to determine through laboratory and greenhouse studies of representative soils of Alabama the effects of lime on the solubility of native soil K, on the fixation of applied K, and on the absorption or utilization of K by plants.

## MATERIALS AND METHODS

### *Description of soils*

Six soils (table 1), representing the major soil areas in Alabama were used in the liberation and fixation studies conducted in the laboratory. These soils

<sup>1</sup> Contribution from the department of agronomy and soils, Alabama Agricultural Experiment Station, Auburn, Alabama. Published with the approval of the director.

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represent the Appalachian Plateau, Coastal Plain, Highland Rim, Piedmont Plateau, and Black Belt regions of the state. The various soils present a wide range in exchange capacity, exchangeable bases, and total K content.

### *General analytical methods*

Exchangeable K in soils was determined by the method of Volk (18) using sodium cobaltinitrite. Filtering crucibles with fritted glass discs of fine porosity were used in lieu of the asbestos-padded Gooch crucible. Exchangeable Ca was extracted from the soils by leaching with neutral normal ammonium acetate and was precipitated as the oxalate and titrated with  $\text{KMnO}_4$ . Exchange capacity was determined by leaching with ammonium acetate and distilling off the adsorbed ammonia into standard acid. The total K of the soils was extracted by digestion with hydrofluoric acid. After removal of the silica, the residue was taken up in dilute HCl, filtered, and made up to volume. An aliquot was taken to dryness and the residue dissolved in distilled water. This solution was then

TABLE 1

*Some characteristics of the six Alabama soils used in the potassium liberation and fixation studies*

SOIL	EXCHANGE CAPACITY	pH	EXCHANGEABLE Ca	EXCHANGE- ABLE K	TOTAL K
	<i>m.e./100 gm.</i>		<i>lbs.*</i>	<i>lbs.†</i>	<i>lbs.†</i>
Hartsells fine sandy loam.....	3.1	5.1	630	57	3,600
Norfolk sandy loam.....	2.9	5.7	800	71	1,600
Dickson silt loam.....	4.0	5.6	1,110	114	2,400
Cecil sandy clay loam.....	4.8	5.7	1,040	146	11,800
Davidson clay loam.....	6.1	6.1	2,640	198	16,100
Sumter clay.....	22.5	7.9	Calcareous	160	8,300

\*  $\text{CaCO}_3$  per acre.

†  $\text{K}_2\text{O}$  per acre.

made distinctly alkaline with NaOH and again evaporated to dryness. Finally the residue was taken up in dilute acetic acid and K determined by the sodium cobaltinitrite procedure described by Volk (18). The HF extraction procedure for determining total K in these soils of low K content was used because of the contamination frequently encountered from the  $\text{CaCO}_3$  which is required in the J. Lawrence Smith fusion method. The pH of the soils was measured by the use of the glass electrode. Plant samples were digested with a mixture of perchloric, nitric, and sulfuric acids (15), and the K was determined by precipitation with sodium cobaltinitrite.

### EFFECT OF LIME ON RELEASE OF NONEXCHANGEABLE POTASSIUM

To study the effect of lime on the solubility of soil K the following procedure was used: Thirty grams of soil was dispersed with 400 ml. of 0.01 *N* acetic acid and leached on a Büchner funnel to remove all exchangeable bases and to saturate the soil complex with H. It was found in preliminary tests that 0.01 *N* acetic

acid would remove approximately the same amount of K from several of the soils used in this study as was removed by normal ammonium acetate. The pH of 0.01 *N* acetic acid was approximately 3.5; it was concluded that any destruction of soil colloids by this mild treatment would be negligible.

After being leached with acetic acid, the soils were washed with distilled water and alcohol, dried, and put in glass tumblers.  $\text{Ca}(\text{OH})_2$  was added in amounts calculated to produce 75 and 150 per cent Ca saturations of the exchange complex. The soils were kept at constant moisture (approximately 30 per cent) and room temperature for 80 days. They were then extracted with dilute acetic acid and saturated with H as before, the leachate being analyzed for K. The soils were again washed, dried, and set up with applications of  $\text{Ca}(\text{OH})_2$ . They were again incubated at constant moisture (70 days), and exchangeable K was determined. The only divergence from this procedure was with Sumter clay, a calcareous soil, which received no applications of  $\text{Ca}(\text{OH})_2$ .

In this study it was found that, without exception, the addition of  $\text{Ca}(\text{OH})_2$  to five acid soils increased the release of nonreplaceable K to an exchangeable form (table 2). Soils that were 75 per cent Ca-saturated released, on the average, 27 per cent more K than did soils that were H-saturated. The 150 per cent Ca-saturated soils released 50 per cent more K than did the unlimed soils. The magnitude of K release was small in some cases, but it must be remembered that several of the soils used in the study were coarse-textured, highly weathered, and relatively low in K-bearing minerals (table 1). The rate of release of K in the Sumter, a calcareous clay, was comparable to that of the fine-textured Davidson, which received a high application of Ca.

Early investigators were primarily concerned with the influence of lime on the water-soluble portion of soil K. More recent investigators (2, 6, 8) have advanced proof or have accepted the belief that exchangeable K is also a plant-available form. Soil chemists now generally agree that K is present in the soil in the following equilibria: nonexchangeable K (primary and secondary minerals)  $\rightleftharpoons$  exchangeable K  $\rightleftharpoons$  water-soluble K. These reactions are displaced to the right by the normal weathering processes, leaching, and absorption of K by plants. The importance of this displacement in supplying growing plants with K was emphasized by Hoagland and Martin (5), who found that a major portion of the K absorbed by a crop may be derived from nonexchangeable forms during the growing season. Lamb (9) also suggested that the rate of solubility of soil K is a better index of availability than is the amount soluble at any given time. Moreover, it is now apparent that plants are able to obtain more K during the growing season than is present at any one time in the exchangeable form in most highly weathered soils. Obviously, any factor that affects the conversion of soil K to an available form is extremely important in plant nutrition.

The results of this liberation study indicate that the addition of lime to a soil would favor the release of nonexchangeable K to replaceable forms. At the same time it would speed up the depletion of the soil's supply of readily soluble K through plant removal, erosion, and leaching processes. In a 4-year study of nutrient losses by erosion, Rogers (13) found that the soil's supply of exchange-

able K was depleted by sheet erosion at a much greater rate than the more difficultly soluble fraction. In view of these facts, it would appear that the ultimate effect of liming on the K status of soils with low K reserves might be much less beneficial than is suggested by any immediate but relatively temporary effect on the release of nonexchangeable K.

#### POTASSIUM "FIXATION"<sup>3</sup> STUDY

For a comparison of the relative K-fixing powers of different soils, it was considered desirable to start with the same degree of Ca and K saturation on all the soils used in this study. To accomplish this, the soils were leached with 0.01 *N* acetic acid until free of all except a trace of Ca. After they were washed free of excess acid and dried, 100-gm. samples of soil were put in glass tumblers.  $\text{Ca}(\text{OH})_2$  was added in amounts calculated to produce 75 and 150 per cent Ca saturation of the exchange capacity. KCl was then added in solution in amounts equivalent to 60 and 300 pounds of  $\text{K}_2\text{O}$  per acre. Control samples without Ca and without K were included. The soils were kept at approximately 30 per cent moisture and room temperature for 80 days. After drying, 30-gm. samples were analyzed for exchangeable K.

#### *Effect of lime on fixation of applied potassium*

To make an exact study of the effect of lime on the fixation of *applied* K in different soils, it would be desirable to remove the original exchangeable K present in the soil and to prevent any release of nonexchangeable K during the period of study. Since the latter cannot be accomplished, it is possible in such a study only to measure the effect of lime on the released as well as on the applied K. Furthermore, since lime does exert a considerable influence on the release of nonexchangeable K, the results of any investigation designed to show the effect of lime on the fixation of applied K represent the over-all effect of lime on applied and native soil K.

Without the information obtained in the K liberation study (table 2), the results of the fixation study (table 3) would be most confusing and misleading. One might easily conclude that lime had no consistent effect on the fixation of added K. That, however, is not considered to be the case. With the Hartsells, Norfolk, and Dickson soils, where relatively small amounts of K were released from nonexchangeable forms as a result of liming, there was evidence of a definite increase in fixation as a result of adding Ca. With the Cecil and Davidson soils, however, it was found that the magnitude of K released as a result of lime applications was greater than, or equal to, any effect of the Ca on the fixation of added K. This resulted in an apparent negative fixation or no apparent significant effects of lime on fixation in these soils. There is no reason to assume that the Cecil and Davidson did not fix K in somewhat the same manner as did the other soils; however, any apparent effect of Ca on the fixation of applied K was overshadowed by the increased release of K from a nonexchangeable form. It is

<sup>3</sup> "Fixation" is considered to mean the conversion of exchangeable or water-soluble K to a nonexchangeable form.

believed that this two-way effect of lime explains the fact that some of the soils failed to show any apparent increase in K fixation with application of lime. It was possible to measure only the net effect of the two reactions operating in opposite directions.

TABLE 2

*Potassium released from nonexchangeable form by six Alabama soils, and percentage of increase in release due to lime applications*

SOIL	Ca SATURATION	K <sub>2</sub> O RELEASED PER ACRE			INCREASE DUE TO LIME
		1st 80 days	2nd 70 days	Total 150 days	
	<i>per cent</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>per cent</i>
Hartsells fine sandy loam	0	26	7	33	..
	75	31	11	42	27
	150	35	16	51	55
Norfolk sandy loam	0	24	8	32	..
	75	29	11	40	25
	150	33	15	48	50
Dickson silt loam	0	35	10	45	..
	75	34	16	50	11
	150	36	21	57	27
Cecil sandy clay loam	0	32	14	46	.
	75	51	18	69	50
	150	55	23	78	70
Davidson clay loam	0	68	20	88	.
	75	77	29	106	26
	150	85	45	130	48
Sumter clay	Calcareous	104	27	131	..

*Effect of rate of applied potassium and exchange capacity of soil on fixation*

Many investigations have shown that almost all soils will fix some applied K, provided a sufficient concentration is added. Results of this study (table 4) support the findings of Seatz and Winters (16) that the higher the application of K, the greater is the percentage fixation. There was no apparent relation between exchange capacity and the amount of K fixed by H-saturated soils. The Hartsells, having one of the lowest exchange capacities of any of the soils studied, fixed a higher percentage of applied K than did any of the other acid soils.

The calcareous Sumter clay was found to fix a higher percentage of applied K than any of the acid soils. Almost one-half of an application of 300 pounds of K<sub>2</sub>O per acre was fixed by this soil.

INFLUENCE OF LIME ON UPTAKE OF POTASSIUM BY PLANTS

In the study of potassium absorption, alfalfa, sericea, and Sudan grass were grown on Hartsells fine sandy loam in the greenhouse. The soil was originally

at a pH of 4.8, and contained exchangeable K and Ca equivalent to 150 pounds of  $K_2O$  and 960 pounds of  $CaCO_3$  per acre, respectively. Nitrogen and phospho-

TABLE 3  
*Influence of lime on fixation of applied potassium*

SOIL	Ca SATURATION	K APPLIED	EXCHANGEABLE K AFTER 30 DAYS	INCREASE OR DE- CREASE IN EX- CHANGEABLE K DUE TO LIME
	<i>per cent</i>	<i>lbs.*</i>	<i>lbs.*</i>	<i>lbs.*</i>
Hartsells fine sandy loam	0	60	70	....
	75	60	67	-3
	150	60	65	-5
	0	300	244	....
	75	300	234	-10
	150	300	229	-15
Norfolk sandy loam	0	60	93	....
	75	60	78	-15
	150	60	72	-21
	0	300	280	....
	75	300	268	-12
	150	300	243	-37
Dickson silt loam	0	60	112	....
	75	60	104	-8
	150	60	97	-15
	0	300	300	....
	75	300	297	-3
	150	300	289	-11
Cecil sandy clay loam	0	60	104	....
	75	60	115	+11
	150	60	103	-1
	0	300	289	...
	75	300	290	+1
	150	300	292	+3
Davidson clay loam	0	60	186	....
	75	60	170	-7
	150	60	219	+33
	0	300	367	....
	75	300	365	-2
	150	300	414	+47
Sumter clay	Calcareous	0	83	....
		60	105	....
		300	206	....

\*  $K_2O$  per acre.

rus were applied in the form of  $NH_4H_2PO_4$  at the rate of approximately 20 pounds of N and 100 pounds of  $P_2O_5$  per acre. Ten pounds of borax per acre was applied

TABLE 4

*Potassium-fixing capacity of soils as related to exchange capacity and rate of applied potassium*

	NORFOLK SANDY LOAM	HARTSELLS FINE SANDY LOAM	DICKSON SILT LOAM	CECIL SANDY CLAY	DAVIDSON CLAY LOAM	SUNTER CLAY
Exchange capacity, m.e./100 gm.....	2.9	3.1	4.0	4.8	6.1	22.5

*Percentage of applied and liberated K fixed in 80 days\**

60 lb./acre K <sub>2</sub> O applied . . .	7.0	27.8	7.4	11.9	1.0	26.5
300 lb./acre K <sub>2</sub> O applied.....	17.6	27.6	16.9	19.1	14.3	46.2

\* All soils were saturated with H in a study to determine their relative K-fixing power. Percentage fixation was calculated as follows: (exchangeable K from control sample with no K added) plus (applied K) minus (exchangeable K from soil receiving K application); this difference was divided by the amounts of exchangeable K from control sample plus applied K.

TABLE 5

*Effect of lime on yields, and amount of potassium removed from Hartsells fine sandy loam by three different crops\**

Applications and results on a per-acre basis

CROP	CaCO <sub>3</sub> APPLIED	K <sub>2</sub> O APPLIED	YIELDS, DRY WEIGHT	K <sub>2</sub> O REMOVED	pH OF SOIL AFTER SECOND CROP	EXCHANGE- ABLE K <sub>2</sub> O PER ACRE AFTER SECOND CROP
	lbs.	lbs.	lbs.	lbs.		lbs.
Sericea (1st cutting)	2000	0	2240	23		
	6000	0	740	9		
	2000	50	2860	33		
	6000	50	1260	18		
Sericea (2nd cutting)	2000	0	1391	..	6.3	66
	6000	0	266	..	7.0	77
	2000	50	2085	..	6.3	139
	6000	50	1220	..	7.0	145
Alfalfa	2000	0	1060	22		
	6000	0	940	16		
	2000	50	1380	30		
	6000	50	1260	28		
Sudan grass (1st cutting)	2000	0	2760	34		
	6000	0	3210	36		
	2000	50	3300	61		
	6000	50	3790	66		
Sudan grass (2nd cutting)	2000	0	3370	15		
	6000	0	2940	14		
	2000	50	3400	29		
	6000	50	3270	29		

\* Two unlimed series (with and without K) were planted to each crop, but all crops were complete failures without lime on this soil, the original pH of which was 4.8.

to the alfalfa. Lime was added in the form of marble dust (a high-Ca stone) 1 week before planting. KCl was used as the source of K.

When mature enough for hay, the plants were cut and dried, and the K content was determined. Exchangeable K in the soils growing sericea was determined at the time of the second cutting.

Evidence of the variable effect of lime on K absorption and yields of different types of crops is presented in table 5. Probably because of nutrient deficiencies associated with the low pH (4.8) of the untreated soil used in this study, all of the crops died shortly after germination on the soils that received no lime (fig. 1). In view of this, the comparisons that follow are between 1- and 3-ton rates of ground limestone on the individual crops and between the three different plants, alfalfa, sericea, and Sudan grass.



FIG. 1. SECOND-GROWTH SERICEA ON HARTSELL'S FINE SANDY LOAM WITHOUT ADDED  $K_2O$

$CaCO_3$  applications per acre: 1 = 0; 2 = 2,000 lbs; 3 = 6,000 lbs.

The 3-ton application of lime had only a slight depressive effect on the yields of alfalfa, but it reduced the yield of the second cutting of sericea to near failure. These results seem logical in view of the findings reported by Bower and Pierre (1) to the effect that such plants as alfalfa, which require a large amount of Ca are able to withstand high Ca:K ratios in the soil. It appears that the reduction in yield of sericea by the 3-ton rate of lime was caused, in part at least, by an unfavorable Ca:K relationship, since the decrease in yield with the addition of lime was overcome somewhat by the application of K (fig. 2). The second growth of sericea nearly died out without K applications where 3 tons of lime were added but made fair growth with the same rate of lime plus  $K_2O$ . It is interesting to note that the soils receiving the high rate of lime and growing K-deficient plants contained slightly more exchangeable K than did the soil in the pots that received less Ca. This is further evidence that the high Ca level in the soil either prevented absorption of K or produced an unfavorable balance in the plant.

The first cutting of Sudan grass showed a definite increase in yields as a result of lime. Yields of the second growth, however, were reduced by the high rate of lime. It appears that Sudan grass, requiring relatively small amounts of K for normal growth, responded to Ca applications until the exchangeable K became somewhat depleted. Then the addition of high rates of lime resulted in Ca:K ratios that were too high for normal growth.



FIG. 2. VALUE OF POTASH IN CORRECTING OVERLIMING INJURY TO SECOND-GROWTH SERICEA ON HARTSELL'S FINE SANDY LOAM

Applications per acre: 2 = 0 lbs.  $K_2O$ , 2,000 lbs.  $CaCO_3$ ; 3 = 0 lbs.  $K_2O$ , 6,000 lbs.  $CaCO_3$ ; 5 = 50 lbs.  $K_2O$ , 2,000 lbs.  $CaCO_3$ ; 6 = 50 lbs.  $K_2O$ , 6,000 lbs.  $CaCO_3$

#### OVER-ALL INFLUENCE OF ADDITIONS OF LIME ON POTASSIUM AVAILABILITY

Recent reviews of the literature dealing with the lime-potash problem (11, 12) have pointed out some of the apparently contradictory results and conclusions that have been reported. Unquestionably, the varied conditions and techniques used in different investigations have tended to cloud the issue. Furthermore, any given set of data may simply add to the confusion unless properly interpreted. With the results of the present study in mind, it is understandable how it would be difficult to predict what results a K-liberation study with soils of varying degrees of initial K saturation might yield if the exchangeable K were not removed from the soil at the beginning of the experiment. Further study is needed to determine whether liming favors the release of nonexchangeable K from a wide variety of soils when subjected to a uniform treatment, including similar initial K saturation. The concentration of K in the soil solution unquestionably would affect the release of nonexchangeable K to more soluble forms. This fact alone may explain the failure of various investigations to show the same effect of lime on the liberation of soil K from different soils.

It is understandable also how this two-way action of lime—favoring the release of soil K but increasing fixation of added K—might produce variable net results in fixation studies with different soils. The fixing power of the soil, as well as the amount and solubility of nonexchangeable K, would affect the net results obtained by the customary procedure for determining fixation.



There appears to be a threefold influence of Ca in (a) increasing the release of nonexchangeable K, (b) causing greater fixation of applied K, and (c) repressing the absorption or efficient utilization of K by plants. Differences in the K needs and Ca:K tolerances of plants, as well as the different K-liberating and K-fixing capacities of soils, present too many variable factors to permit generalizations.

#### SUMMARY AND CONCLUSIONS

Laboratory and greenhouse experiments were conducted with six Alabama soils to determine the influence of lime on the release of nonexchangeable soil K, on the fixation of applied K, and on the absorption and utilization of K by plants. The results of these tests may be summarized as follows:

The addition of Ca resulted in an increased release of nonexchangeable K on every soil studied. The release of K due to lime was relatively small on some of the coarser-textured soils, which were low in total K content.

Lime increased the fixation of applied K on the coarse-textured Hartsells, Norfolk, and Dickson soils. The Cecil and Davidson soils, which were found to liberate relatively large amounts of nonexchangeable K, appeared to fix no K as a result of lime. It was pointed out that this apparent difference in the effect of lime on fixation in the different soils was due to the magnitude of K released from nonexchangeable forms during incubation by the two groups of soils, the released K masking any effect of lime on fixation in the Cecil and Davidson soils.

Sudan grass and alfalfa appeared to be more tolerant of wide Ca:K ratios than did sericea. In the case of sericea, there appeared to be a definite influence of Ca in repressing the utilization of K, since the soils on which the K-deficient plants were grown contained at least as much exchangeable K as the corresponding soils that received a lower rate of lime.

It would be extremely difficult to generalize as to the overall influence of lime on the available supply of K in the soil. The addition of lime to a soil could result in an increase or a decrease in available K, depending on the ability of the soil to fix applied K and on the kind, amount, and solubility of K-bearing minerals in the soil. The net result of liming must also take into account the varying abilities of different plants to tolerate wide Ca:K ratios.

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# THE IMPORTANCE OF SODIUM FOR PLANT NUTRITION: IV. INFLUENCE OF NITRATE FERTILIZERS ON THE EQUILIBRIUM OF CATIONS IN FODDER BEET

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Because of the relation of sodium to other plant nutritive elements and the somewhat indefinite reactions of the plant, special care must be exercised in describing the function of sodium in the plant. Earlier papers in this series (7, 8) pointed out the difficulty of judging the sodium effect when considered as an individual problem and the necessity for studying it, instead, in the broader light of the equilibrium of cations. Pot trials, designed to investigate how potassium, sodium, and calcium mutually influence growth, indicated that in beets the sodium effect should be interpreted as a primary function rather than as a secondary one. Although a *specific* effect of sodium on the plant cannot be demonstrated, since lack of sodium does not produce characteristic deficiency symptoms, this element appears to be essential for proper plant development.

Practical field trials, carried out in Holland in 1937 and 1938 (5, 14), lent support to the theory that sodium is of special value to the beet. Unfortunately, those who dealt with the results of these trials overlooked some obvious conclusions. Van Itallie, for example, analyzed the plant material only for potassium and sodium, and consequently he could not verify the calcium effect, which would have been desirable for the comparison between sodium nitrate and calcium nitrate. In the further treatment of the trial results, De Willigen suggested that, in practice, K and Na may be considered to have the same effect on beets. As a matter of fact, it would have been difficult for either author to make a sharp distinction between the actions of K and Na, because in all the trials potash salt (40 per cent  $K_2O$ ) containing, theoretically, up to 36 per cent NaCl was used.

On humus sandy soil in 10 fields, beets almost invariably showed a strong reaction both to K and Na applications. On clayey and sandy clay soils, the reactions were not so marked because of the buffer effect, but this alone brought a noteworthy fact to light. Of the 19 trials on clayey soil, in which a comparison was made between nitrate of lime or "kalkammonsalpeter" and Chilean nitrate of soda, with increasing quantities of 40 per cent potash salt, 13 showed no reaction, or only a slight reaction to K. In these same experiments, the number of weak or questionable reactions to sodium, measured by the difference in effect between nitrate of lime and Chilean nitrate of soda in the low-K plots, was only 5. This does not justify the unqualified conclusion that the effect of Na is greater than that of K in most instances, because the balance of ions also depends largely on the Ca ion.

The problem may be illustrated by a yield curve of one of the field trials, typical of the normal trend of the yields on sandy soil (fig. 1). The yields from the

use of Chilean nitrate of soda and nitrate of lime are shown here against the number of kilogram-equivalents  $K + Na$ , applied in the form of nitrate of soda or 40 per cent potash salt. The low  $K$  levels are at the left. It is obvious that  $K$  shortage cannot be met solely by  $Na$ . On the other hand, as the  $K$  increases, the nitrate of lime curve reaches an almost stable level before the point of maximum yield is attained. The latter point is reached only in the presence of adequate sodium (Chilean nitrate of soda curve), indicating that the sodium cannot be replaced by  $K$ . The action of  $K$ ,  $Na$ , and  $Ca$  cannot be distinguished further in this graph. For this, another method is required.

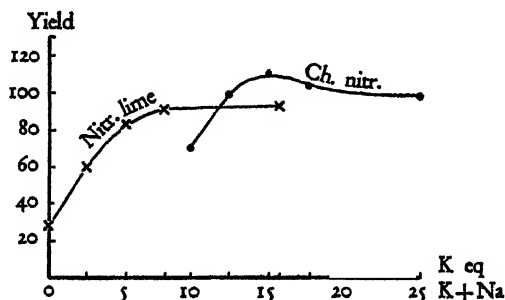


FIG. 1. TRENDS OF BEET YIELDS WITH CHILEAN NITRATE AND NITRATE OF LIME, WITH INCREASING QUANTITIES OF 40 PER CENT POTASH SALT

#### EXPERIMENTAL

To provide a more adequate experimental basis for the investigation, a few new field trials were carried out in 1940 and 1942. In these, the  $K$  additions were made in the form of potassium chloride to eliminate the complications of sodium chloride. A comparison was made between Chilean nitrate of soda and nitrate of lime, each with increasing applications of  $K$ . In addition, a series of plots was included with nitrate of lime plus a quantity of  $NaCl$  corresponding to that contained in the Chilean nitrate of soda dressing. The applications per hectare were as follows:

*In 1940*—800 kgm. Chilean nitrate of soda; 800 kgm. nitrate of lime; and 800 kgm. nitrate of lime plus 530 kgm.  $NaCl$  ( $P$  added in the form of superphosphate);  $K$  additions of 0, 125, 250, 375, and 625 kgm.  $KCl$ .

*In 1942*—1000 kgm. Chilean nitrate of soda; 1000 kgm. nitrate of lime; and 1000 kgm. nitrate of lime plus 660 kgm.  $NaCl$  ( $P$  added in the form of basic slag);  $K$  additions of 0, 150, 375, 625, and 1000 kgm.  $KCl$ .

Table 1 shows the soil analyses of the fields, all on sandy soil. The results are presented according to the method previously adopted (8), in which the dry-matter yields of the plants are shown in triangular graphs against their composition,<sup>1</sup> expressed in ion contents, shown as percentages of the total number of milliequivalents of the three cations absorbed per 100 gm. dry matter.

<sup>1</sup> For full details see (9).

Although objections may be raised to this method,<sup>2</sup> the following advantages are, in our opinion, more important:

The composition of the plant may be taken as the resultant of the actions of the ions adsorbed in the complex and of the fertilizers; otherwise, these must be accounted for separately.

Physiologically, the growth of the plant may be explained as a function of its composition.

Irregularities in the fields, insofar as they affect the plan of the experiment, are corrected automatically in the composition of the plant.

As the maximum yield differed in the four fields (depending on other growth factors), a "top yield" was adopted for each field. This could be deduced from the points lying in the area of the highest yields. All yields are expressed as percentages of these "top yields." The various figures show, at a glance, the rela-

TABLE 1  
*Soil analyses of four experimental fields on humic sandy soils*

LOCATION, DATE	K	Na	WATER-SOLUBLE PHOSPHATE	PHOSPHATE SOLUBLE IN CITRIC ACID	ORGANIC MATTER, LOSS ON IGNITION	pH	FRACTION SMALLER THAN $2\mu$
	m.e.*	m.e.*	p.p.m.	p.p.m.	per cent		per cent
Vinkel, 1940	0.10	0.12	2	49	1.7	6.9	3.2
Schayk, 1940	0.16	0.08	5	45	4.1	5.8	3.4
Vinkel, 1942	0.27	0.12	2.5	43	5.2	6.3	1.6
Halle, 1942	0.41	0.38	2	43	4.4	6.3	2.4

\* Per 100 gm. soil.

tion between yield and composition. The division of the yields in areas is such that the border lines indicate yields of 50, 70, 80, and 90 per cent for the foliage and 25, 50, 75, and 95 per cent for the beet. The different position of the cation equilibrium for foliage (fig. 2) and for the beet (fig. 3) must be attributed, in the main, to a higher Ca content in the foliage and to a higher K content in the beet. Otherwise, it is striking to see the wide limits within which the composition of the beet plant can move. This is even more apparent in figure 4, showing the average composition of the beet plant against the total yield (beet and foliage). It is evident, however, that this accommodating nature of the plant in respect to the mineral composition does not leave its physiology untouched and that an optimal development is closely related to a correct position of the cation equilibrium.

From a physiological point of view, these figures demonstrate that the effect of the univalent ions (K and Na) on the plant cannot be considered as an independent process in which only the quantities count—an idea which is fundamental for all "reaction or yield curves." The bivalent ions also must be considered, and then the Ca ion may easily have a depressive influence on beets. The weight of this influence is determined by the ratio in which bivalent and univalent ions are present.

<sup>2</sup> See 'Discussion.'

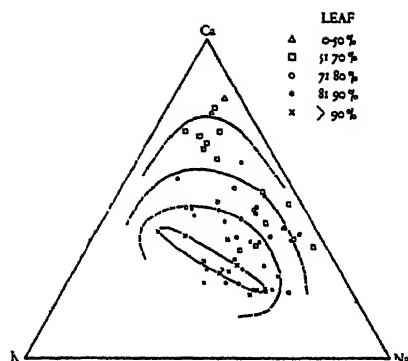


FIG. 2

FIG. 2. RATIOS OF K, Na, AND Ca IN THE FOLIAGE OF FODDER BEETS IN RELATION TO YIELD

Yields are expressed as percentages of "top yield," adopted for each field

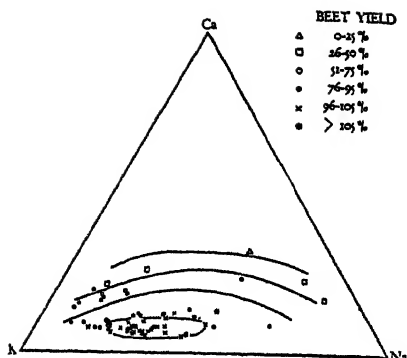


FIG. 3

FIG. 3. RATIOS OF K, Na, AND Ca IN THE BEET ROOT IN RELATION TO YIELD

Yields are expressed as percentages of "top yield," adopted for each field

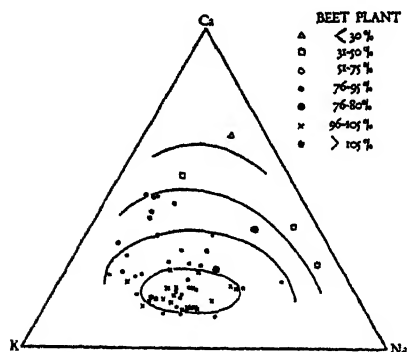


FIG. 4

FIG. 4. AVERAGE COMPOSITION OF THE BEET PLANT IN RELATION TO TOTAL YIELD

Yields are expressed as percentages of "top yield," adopted for each field

FIG. 5. SCHEMATIC RELATION BETWEEN AVERAGE COMPOSITION AND TOTAL YIELD OF FODDER BEET PLANTS

The dots refer to plots without K additions on two trial fields which were poor in sodium. "Fertilizing lines," connecting these points with the point of origin of the K angle show the approximate trend of the composition with increasing KCl additions. Nitrate of lime tends to give low or moderate yields, even with heavy applications of KCl. The Chilean nitrate line cuts the area of very high yields. Addition of NaCl to nitrate of lime gives an intermediate position. The encircled dots indicate the composition of plants grown on the plots without K additions at Vinkel and at Schayk in 1940.

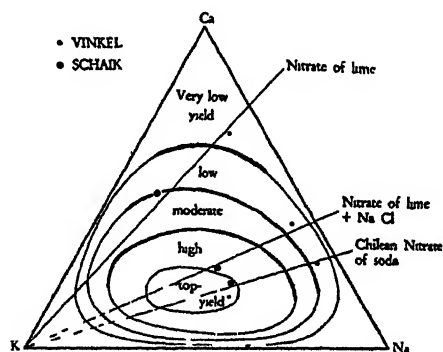


FIG. 5

With regard to the mutual replacement of K and Na, we also reach a somewhat different conclusion from that of earlier investigators. Potassium and sodium

cannot be considered as equivalent nutritive components over the whole range of ratios. It is common experience that an acute potassium shortage cannot be overcome exclusively by abundant sodium. At most, sodium can lessen the deficiency symptoms in such an event.

Not so obvious is the conclusion to be drawn especially from figure 5, that *when an extremely low sodium level prevails, the yields, likewise, remain below the maximum, even when attempts are made to overcome an eventual "shortage of univalent ions" by liberal applications of potassium.* According to the current concept, sodium is a substitute for potassium, though not entirely equivalent to potassium; in fact, some authors refer to applications of sodium as a "camouflage of K deficiency." In contrast, we hold the view, based on the foregoing results, that a more nearly *independent* role must be attributed to sodium in the beet plant. This implies that sodium, like potassium and calcium, is essential for

TABLE 2

*Amounts of primary and secondary cations, supplied by fertilizers, in comparison with those present in exchangeable form in the soil*

Amounts of cations in kilo-equivalents per hectare

LOCATION DATE	EXCHANGEABLE K AND Na IN SOIL		FERTILIZER ADDITIONS	
	K	Na	K (maximum)	Na or Ca
Vinkel, 1940	3	3.5	8.4	9.5
Schayk, 1940	5.1	2.5	8.4	9.5
Vinkel, 1942	8.1	3.6	13.4	12
Halle, 1942	12.3	11.4	13.4	12

proper development of the beet plant. In this connection it should be noted that the need for calcium by the beet is not evident in our figures.

From a practical point of view, several other conclusions can be drawn from the triangular figures. Hudig and Lehr (4) have pointed out that the buffer capacity of soil is overestimated as a rule and that normal fertilizing adds so many "secondary ions" that the result is a considerable movement of the cation equilibrium in the soil. The four fields in our experiments originally contained 3 to 12.3 kilo-equivalents K and 3.5 to 11.4 kilo-equivalents Na per hectare; the fertilizers added contained 8.4 to 13.4 kilo-equivalents K and 9.5 to 12 kilo-equivalents Na or Ca (table 2).

The influence of the secondary ions may be deduced from figure 5, in which the limits shown in figure 4 have been completed according to the most probable trend. Moreover, this figure indicates the composition of the plants grown on the plots without K additions at Vinkel in 1940 and at Schayk in 1940. The lines connecting these points with the K corner point show approximately how the composition of the beet changes with ascending KCl applications. It appears that on these buffer-poor soils, nitrate of lime produces a "fertilizing line" entirely different from that of Chilean nitrate of soda. For nitrate of lime, the line crosses the area of moderate yields and continues across the areas of low and very low



yields. Excessive KCl applications do not increase the chances of good yields. (Compare also figure 1.) The line for nitrate of soda immediately enters an area of better yields and the KCl line moves largely in the area of the highest yields. Apart from the fact that an appreciable saving can be made by adding potassium with nitrate of soda, the latter nitrogen fertilizer, in general, provides better chances of high yields. This applies also to less extreme cases and to more strongly buffered soils (5, 14).

The NaCl effects a considerable improvement over nitrate of lime alone, yet the yield appears not to equal that obtained with nitrate of soda. This can be explained on the grounds that the Ca ions of the nitrate of lime also affect the composition of the plants. With the smaller additions of KCl, especially where NaCl was included, the beet yield fell below that obtained with nitrate of soda. Moreover, from the practical standpoint, the high salt concentration made germination difficult, and an uneven stand resulted

#### DISCUSSION

Many investigations indicate that nitrate of soda usually is superior to calcium nitrate as a fertilizer for beets (3, 6, 10, 11, 13, 14), a result that must be attributed solely to the difference in effect between the Na and the Ca ion. The difficulty in appraising this fact lies, not so much with the demonstration of the agricultural effect, which is unquestionable, but rather with the exact interpretation of its physiological importance. Several decades ago, Stoklasa (12) pointed out the importance of sodium to the sugar beet; in fact, he considered sodium one of the *indispensable nutritive elements*. The nature of his experiments, however, was not such as to assure the indisputability of his conclusions.

We have endeavored to solve the problem by providing an experimental basis in which the effects of the various factors were differentiated as sharply as possible and by adopting a working method which would demonstrate the effects of the factors individually as well as in their mutual relationships. Thus, considerable light can be thrown on the subject, if too great importance is not attributed to the triangular graphs. The object of such graphs is not to give a fixed geometric picture of the yield laws. Our aim is to give only an idea of the interaction of the various closely related nutritive components.

Although Mitscherlich curves are based primarily on the effect of *absolute quantities* of one nutritive element, other factors remaining constant, the accent in the triangular graphs is on the *ratios* of the various nutritive elements. These must be deemed at least as important as their absolute quantities. That it is almost impossible to modify one factor, while keeping all the other factors constant, follows from the fact that a nitrogen fertilizer also carries "secondary ions," which may influence the whole cation equilibrium. This equilibrium, which in the Mitscherlich concept represents part of the "fertility level," appears from figure 5 to be definitely unstable.

Meanwhile we realize that, even though the ratios are as favorable as possible, the absolute quantities play a role. In our view, the primary object of fertilizing must be to obtain correct ratios, thus making use of the natural fertility of the soil, so as to benefit best by the circulating nutritive matter and the fertilizers.

Accordingly, the situation of the adsorbed ions at the adsorptive complex (part of the fertility level) must determine the *minimum* fertilizer requirements to obtain the correct equilibrium. On the Dutch sandy soils, which are naturally low in mineral nutrients for plants, fertilizers in excess of this minimum are often applied to increase production. Although in this instance these increased quantities result in heavier yields, one must not lose sight of the fact that, as a consequence, the natural balance of the soil may be subject to far-reaching changes, such as those experienced in our trials. As to the connection between ratios and absolute quantities, too few facts are as yet available to warrant detailed discussion of the matter.<sup>3</sup>

Obviously, a triangular graph allows comparison of only three components, for which we selected the three most important cations. Magnesium, which requires further consideration, appears, at first glance, to have little influence on the results. When the relative contents of Ca + Mg are substituted for Ca alone in figures 2 and 3, there is a general upward displacement of the points with no change in their relative position or in the shape of the yield areas. Other factors, such as the N and P supplies, may have some influence on the shape and position of the yield areas.

The foregoing field experiments constitute, in a sense, a completion and control of the dusarite pot trials previously described (8). The pot trials included only a limited number of K additions; the field trials included much higher K additions, as a result of which a larger part of the K—Na—Ca triangle is filled. On the whole the results are in agreement, although there are points of difference. For the foliage, the highest yields in the pot trials were found to lie considerably closer to the Na angle of the triangle than in our field trials. This difference is probably due to the difference in nitrogen supply, which is usually larger in pot trials than in field trials. Increased nitrate absorption is coupled with increased cation absorption. The foliage from the pot trials (7, 8) was often found to contain more than double the quantity of cations determined in field trials. In the beet there were no systematic irregularities in this respect. Not only may plant variety differences play a part, but in the field the foliage is subject to leaching, as a result of which univalent ions (K, Na, Cl), in particular, may be lost. Such leaching does not occur, of course, in pot trials in greenhouses.

Finally, mention should be made of the rather arbitrary choice of the final composition of the beet, that is, the composition at the time of harvest. In our opinion, the composition is both *cause* and *effect*—cause, because it determines the physiology and growth of the plant. It would be more rational, therefore, to distinguish growth periods, in which the growth is related to the composition at the beginning of the respective period, according to the plan advanced by Boonstra (1, 2). This method, of course, is too laborious for complicated fertilizer experiments. In our opinion, it would be preferable to draw a number of plant samples in the period of maximum growth (at about the beginning of August), the mineral composition of which could be used as a standard in addition to, or instead of, the final composition of the beet.

<sup>3</sup> The intervening war prevented the continuation of our investigations in this direction.

## SUMMARY AND CONCLUSIONS

Field trials in 1940 and 1942 gave further evidence that potassium and sodium can only partly assume one another's functions in the beet plant. Sodium seems to be essential for maximum production, and the effect of very heavy additions of KCl is, therefore, limited on Na-poor soils. The experiments confirm the theory that calcium often has a bearing on yield. In practice, nitrate of soda may, therefore, be preferred to nitrate of lime.

Plotting the yield and the composition of the beet against each other in triangular graphs provided an over-all picture of the effect of the cation equilibrium. On the basis of these figures, the importance of the ratios of the nutritive ions, as reflected in yield curves, has been discussed in comparison with the effect of the absolute quantities.

The different influences of the nitrate fertilizers on the cation equilibrium were also demonstrated in a triangular graph. This showed that NaCl added to nitrate of lime produced results superior to those of nitrate of lime alone but inferior to those of Chilean nitrate of soda.

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